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Quantitative Analysis

BOOK III

By

I.C.S. STAFF

QUANTITATIVE ANALYSIS

Parts 5-7

378

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QUANTITATIVE ANALYSIS

(PART 5)

Serial 201E

Edition 2

IRON ANALYSIS

GENERAL REMARKS

1. Thus far the work in quantitative analysis has been confined to the determination of single elements in chemical compounds of known composition, and to the complete analysis of substances, in both of which cases a student could check his work: in the first instance, by calculating the theoretical percentage of the element sought, in the compound analyzed; and in the second, by adding together the percentages of the different constituents found, to see how near the sum of the constituents approaches 100 per cent.

In *Quantitative Analysis*. Parts 1 and 2, we endeavored to describe the most approved methods of determining the principal elements in a way that would give the student a good general idea of the methods of quantitative work, and, at the same time, some experience in the determination of the elements most frequently met. In Parts 3 and 4, the knowledge obtained in Parts 1 and 2 is put in practice in the analysis of a few typical compounds, alloys, and minerals, chosen with a view to rendering the student familiar with the general methods of analysis.

In a work of this character it would be impossible to

describe the analysis of every existing compound, alloy, and mineral, and no attempt has been made to do so. Instead of this, we have attempted, by means of a few typical examples, to render the student so familiar with the different processes that he can readily apply his knowledge in all similar cases; and, if he has worked faithfully on his papers up to this point, he should now be able to analyze any compound, alloy, or mineral likely to be met.

The following work, which deals with technical analysis, is built up largely on the same principles as the preceding, but differs from it in several respects. As a rule, a complete analysis is not required, but merely the determination of some of the constituents, generally those on the percentage of which the value or quality of the substance depends. Hence, in much of the succeeding work the accuracy of the results cannot be determined by the methods previously employed, and, except in the case of determinations that are made daily, the results should always be checked by making duplicate determinations. In the laboratories of manufacturing establishments where a chemist determines the same elements in many samples every day, it would generally be impossible to make duplicate determinations in each case, and it is hardly necessary, for he soon becomes so familiar with his routine work that he is not likely to make a mistake; but even in these cases, it is a good plan to make duplicate determinations if time permits, and any determination outside of the regular work should always be checked by a duplicate.

So many methods are employed in iron and steel works chemistry at the present time that it would be impossible to describe them all in this Paper. Consequently, only one or two methods, as a rule, will be given for the determination of each element. In the case of elements for the determination of which several methods are largely employed, one strictly accurate method and one or two of the more rapid methods will generally be described. In experienced hands most of these short or rapid methods will yield extremely accurate results with most samples, and, on account of their

rapidity—enabling a chemist to do a great deal of work and to obtain results in a short time—they are used almost exclusively in iron and steel works laboratories. As some of them do not give accurate results in all cases, it is necessary for the iron-works chemist to be familiar with longer methods that will yield exact results in every case, and, for this reason, both short and long methods are described.

IRON ORES

2. As iron ore is the principal “raw material” in the manufacture of iron, its analysis will be treated first. This is an important matter, for the value of the ore depends on its composition. Other things being the same, the value of an ore depends on the amount of iron it contains, but the percentage of iron is not the only consideration, for other constituents have much to do with fixing its value for certain uses. Thus, an ore containing much phosphorus, however rich in iron it may be, would be unsuited for the production of pig iron to be used in the manufacture of Bessemer steel, because the phosphorus in the ore would pass into the steel and render it unfit for use.

An analysis is not only useful in determining the value of an ore, but also to determine the quantity of other material that is to be charged into the furnace with it. Thus, the amount of limestone added to form a slag with impurities depends on the amount of impurity to be “slagged off.” The principal determinations in the analysis of iron ores are *insoluble matter* and *silica*, *iron*, *phosphorus*, *sulphur*, *manganese*, and sometimes *water*.

3. **Selection and Preparation of a Sample.**—The selection of a sample is a matter of importance, for, if the results of the analysis are to be of any value, a sample must be chosen that accurately represents the whole quantity of which the analysis is supposed to show the composition.

In order to obtain such a sample, the following points

should be observed: the relative amount of fine ore and lumps in the lot to be sampled should be carefully noted, and this proportion must be observed in the sample taken. In sampling lumps, it is not sufficient to break pieces from the surface, but the lump should be broken, and pieces taken from both the exterior and interior, for a lump seldom has the same composition throughout. As the heavy particles that naturally find their way towards the bottom seldom have the same composition as the lighter material near the top, portions of the sample should be drawn from different parts of the lot. The fine ore should be taken up in portions amounting to about a teaspoonful, and the pieces of lumps should be about the size of cherries.

This sample will usually be too large for laboratory use, and a smaller sample must be obtained from it. Just how this is done is not a matter of importance so long as the sample obtained represents the composition of the whole quantity, but probably the best method, and the one most frequently used, is that known as quartering. This is accomplished as follows:

Break up the lumps of ore until the largest pieces are about the size of buckshot, mix the whole sample thoroughly, place it in a conical pile, and then flatten this pile. Mark the pile into quadrants, by means of a stick, as shown in Fig. 1, by passing two lines at right angles to each other through the center of it. Then remove two alternate quarters and throw them aside. Thus considering the quadrants as numbered consecutively from 1 to 4, Nos. 1 and 3 would be discarded, and Nos. 2 and 4 saved, or vice versa.

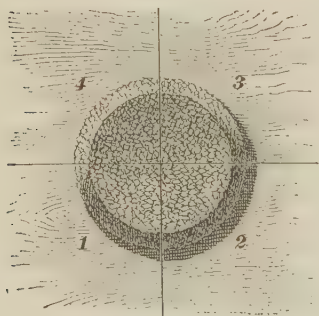


FIG. 1

The quadrants to be discarded may be removed by means of a spatula, shown in Fig. 2. The quadrants left are now thoroughly mixed, made into a conical pile, and the operation is repeated until a sample

of suitable size for the laboratory is obtained. If the sample contains lumps of sufficient size to cause danger of getting a final sample that does not represent the whole lot of ore, it should be broken up finer during the operation. When a sample of the proper size is obtained, it is ground to



FIG. 2

a coarse powder and mixed thoroughly. Although a cast-iron mortar and pestle are largely used in breaking up and grinding iron ores, they are totally unfit for this purpose, for the iron, especially of the pestle, rapidly wears away, and, becoming mixed with the ore, gives it a fictitious value in iron. A mortar and pestle of hardened steel, or a chilled-iron bucking board and muller, shown in Fig. 3, answer the purpose much better.

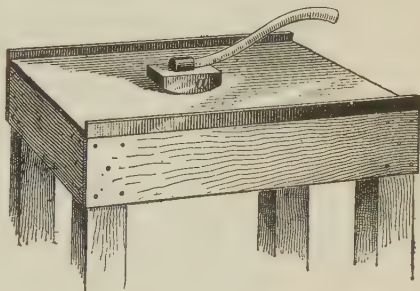


FIG. 3

The treatment of the ore from this point on differs in different laboratories. Some furnacemen want to know the exact composition of the ore as it is purchased and charged into the furnace, while others want to know the composition of the dry ore, and the chemist must regulate his method of treatment to suit the particular case. The following method probably gives the most thorough knowledge of the composition of the ore, but where such complete knowledge is not desired, the treatment may be shortened. In any case, if the moisture is to be taken into account, the ore should be ground and quartered quickly, as wet ores will lose some of their water during the operation, if much time is spent, and dry ores may take up some moisture from the atmosphere.

WATER

4. Determination of Hygroscopic Water.—Spread the ore out on a clean piece of paper, and weigh about 50 grams of it into a watch glass or other suitable vessel, dipping portions from different parts of the sample by means of a spatula. Care should be taken to dip to the bottom of the sample each time, for however well mixed it may be, this coarsely powdered sample will scarcely be uniform, the heavier portions that tend to sink to the bottom seldom having the same composition as the lighter portions on top. Place the weighed sample in an air bath, and heat it at a temperature ranging from 100° to 105° C., until it ceases to lose weight. To be sure of obtaining accurate results, this drying should be continued for 10 or 12 hours, though in many cases the water will all be driven off in much less time. When a constant weight is obtained, the loss in weight is the weight of hygroscopic water, and from this the percentage of water in the sample is obtained.

If only an analysis of the dry ore, or of the ore as it comes from the mine, is required, this determination may be omitted, and the other determinations proceeded with, either at once, or after drying, as the case may be. If this method is followed, however, by working on the same sample after it is dry, the percentage of water in the original sample and the percentage of other constituents in the dry ore are obtained; and, from these figures, the percentage of each of the constituents in the wet ore may readily be calculated.

INSOLUBLE MATTER AND SILICA

5. Grind the sample used for the determination of water in an agate mortar until it is fine enough to pass through a sieve having 100 meshes to the linear inch, commonly called a 100-mesh sieve. The whole must be passed through the sieve, for the hard particles that resist crushing seldom have the same composition as the easily pulverized portion. As soon as powdered, the sample should be placed in a bottle and tightly stoppered.

Weigh 1 gram of this sample into a porcelain dish, add 20 cubic centimeters of concentrated hydrochloric acid, cover the dish with a watch glass, and boil very gently on a hot plate or sand bath until the ore appears to be completely decomposed. A hot plate is merely a thin iron plate placed on a suitable support and heated by a burner; and a sand bath is made by placing some sand in an iron basin and heating it in the same way.

When the sample appears to be decomposed, remove the watch glass, wash any particles that may have spattered on it back into the dish, and evaporate to dryness. Or, if the solution has a tendency to bump, evaporate to dryness with the watch glass on. This requires more time, but is necessary in some cases to avoid loss by spattering. When dry, heat the residue until the odor of hydrochloric acid is no longer given off, but avoid a very high temperature. Allow the residue to cool, add about 10 cubic centimeters of concentrated hydrochloric acid, and boil for a few moments. Then add 30 or 35 cubic centimeters of water, and continue the boiling for a few minutes to dissolve all the soluble matter. Filter, preferably with suction, wash thoroughly with dilute hydrochloric acid and water alternately, and, finally, two or three times with water. Suck the precipitate and filter as dry as possible, wrap the filter around the precipitate, place them in a platinum crucible, and, after heating gently to drive off moisture and char the paper, ignite intensely over the blast lamp. Allow the crucible to become cool, and weigh as *insoluble matter* or *silicious residue*, as it is sometimes called.

To the insoluble matter in the crucible, add about ten times its weight of "fusion mixture," made by mixing equal parts of the carbonates of sodium and potassium, and heat over the blast lamp till all is in a state of quiet fusion. Run the fusion well up on the sides of the crucible, and then cool it rapidly by dipping the crucible into a porcelain dish containing about 50 cubic centimeters of pure cold water, taking care not to get any water in the crucible at first. When the fusion becomes cool enough so that there is no further danger

of spattering, turn the crucible on its side, cover the dish with a watch glass, and heat to boiling, so as to partially dissolve the fusion. Remove the dish from the flame, and complete the solution by cautiously adding concentrate hydrochloric acid until the liquid has a strong acid reaction. Remove the crucible, wash it off thoroughly, letting the washings run into the dish, evaporate to dryness on a sand bath or hot plate, and heat at a moderate temperature to render the silica insoluble. When cool, add 10 cubic centimeters of concentrate hydrochloric acid and 30 or 40 cubic centimeters of water to the residue, and boil a few minutes to dissolve the soluble matter. Filter and wash thoroughly with hot water to remove all alkaline salts from the filter. Wrap the filter around the precipitate, place them in a platinum crucible, and, after heating gently to expel moisture and char the paper, ignite intensely over a blast lamp. Cool, and weigh as silica SiO_2 .

IRON

6. There are two methods of determining iron in ores in very general use, known as the bichromate and the permanganate methods. The permanganate method gives a very distinct end reaction, but as permanganate is decomposed by hydrochloric acid or chlorine, precautions must be taken to render harmless the hydrochloric acid used to dissolve the ore, before titrating the solution. Hydrochloric acid and chlorine do no harm when the bichromate method is used; hence, the ore may be dissolved in hydrochloric acid, the solution reduced by stannous chloride, and this may be titrated at once with bichromate. As each method has its advantages, they are both largely used. A method of dissolving an ore in hydrochloric acid, reducing with stannous chloride and titrating with permanganate, has recently been devised, and is being quite largely used at the present time, in some places. As it has several advantages, it will probably be more generally adopted in time, and consequently all three methods will be described.

7. The Bichromate Method.—Weigh 1 gram of the sample into a beaker, add 20 or 25 cubic centimeters of concentrate hydrochloric acid, cover the beaker with a watch glass, and digest on a sand bath for several hours, at a temperature very near the boiling point, until the ore appears to be completely decomposed. From .2 to .5 gram of potassium chlorate is frequently added at this point to oxidize any organic matter that may be present. Now raise the temperature and boil the solution very gently until its volume is reduced to about 10 cubic centimeters. With nearly all ores, the iron will now be completely dissolved, and the residue will be light colored. It should be examined, however, and if reddish, or very dark, it should be treated as described later.

If the residue is white, remove the watch glass and wash it off into the beaker, washing down the sides of the beaker at the same time, and using a quantity of water about double the volume of the solution. Then slowly add a solution of stannous chloride from a pipette or burette to the hot solution until it is colorless, indicating that the iron is all reduced to the ferrous condition, and add 2 or 3 drops in excess to be sure that reduction is complete.

After a little experience has been acquired, it is easy to tell by the appearance of the solution when reduction is complete, but at first it is best to test the solution by means of potassium sulphocyanide. To do this, place a drop of potassium-sulphocyanide solution on a white porcelain plate, known as a *spot plate*, dip a small drop of the iron solution from the beaker on the end of a stirring rod, and mix it with the drop of sulphocyanide on the plate. If a red color is produced, it shows that the solution still contains ferric iron, and more stannous chloride must be added. If it shows no color, or only a faint pink tint, the reduction is complete.

Pour the reduced solution into a rather large beaker, wash the small beaker thoroughly, adding the washings to the solution, and dilute this to 300 or 350 cubic centimeters with pure cold water. Then add about 25 cubic centimeters of a saturated solution of mercuric chloride all at once, stir the

solution, and titrate with potassium bichromate, running the bichromate in until a drop of the solution, removed to a spot plate by means of a stirring rod, and mixed with a drop of pure potassium-ferricyanide solution, does not produce a blue color for 20 or 30 seconds. The operation should be conducted as rapidly as possible from the time the iron is reduced, for, if allowed to stand for any considerable time, it will be partially reoxidized by the action of the air.

The mercuric chloride is added to destroy the excess of stannous chloride, which, if left free in the solution, would reduce some of the bichromate, and thus yield an erroneous result. If it is added quickly, as directed, it will form a white, silky precipitate that does not in any way interfere with the titration, but if added gradually, a gray or black precipitate of metallic mercury is produced, and the solution must be thrown away, for such a solution will not yield reliable results. If the bichromate is standardized so that 1 cubic centimeter oxidizes .01 gram of iron, and exactly 1 gram of sample is taken, each cubic centimeter of the solution used will represent 1 per cent., and each tenth of a cubic centimeter will represent one-tenth of 1 per cent. of iron in the sample. Many chemists, however, prefer to standardize the bichromate solution so that 1 cubic centimeter of it oxidizes .005 gram of iron; and when this is done, .5 gram of ore is usually taken for the determination. If this is done, the reading in cubic centimeters will represent the percentage of iron, the same as in the first instance.

If the residue left when the ore is dissolved is strongly colored, and exact results are required, the following method should be employed: Dilute the solution slightly so that the hydrochloric acid will not destroy the paper, filter, and wash, receiving the filtrate in a beaker, which should now be covered and stood aside. Place the filter and residue in a platinum crucible, burn off the paper and fuse the residue with about ten times its weight of mixed carbonates of sodium and potassium. Dissolve the fusion in water and hydrochloric acid, filter out the insoluble matter, and wash thoroughly with dilute hydrochloric acid and water. Heat the filtrate

to boiling, add a few drops of concentrate nitric acid, and precipitate the iron with a slight excess of ammonia. Filter, dissolve the precipitate in a mixture composed of equal parts of concentrate hydrochloric acid and water, and add this solution to the main solution of iron. Heat this nearly to boiling, reduce it with stannous chloride, dilute with water, add mercuric chloride, and titrate with bichromate as directed above.

8. The Ordinary Permanganate Method.—Weigh 1 gram of the dry, finely powdered ore into a beaker, add 15 or 20 cubic centimeters of concentrate hydrochloric acid, cover the beaker with a watch glass, and digest on a sand bath or hot plate at a temperature very near the boiling point, until the ore appears to be completely decomposed. This may be accomplished in 15 or 20 minutes, or may require several hours, depending on the ore. If time permits, the sample is generally allowed to digest for several hours in any case to insure complete decomposition. If the ore contains organic matter, a little potassium chlorate should be added to destroy it, and some chemists add it to all ores as a precautionary measure. Probably the majority of ores yield all their iron to this treatment, but if the insoluble residue contains iron, it must be filtered off, fused, and treated as in the determination of iron by the bichromate method.

When decomposition is complete, unless the bulk of solution is considerably reduced, it should be boiled gently until the volume of the solution amounts to rather less than 10 cubic centimeters. Violent boiling should be avoided, as some ferric chloride may thus be volatilized from a concentrate solution. Dilute the solution with about 30 cubic centimeters of water, and, if a large residue remains, it is generally filtered off, washed thoroughly with hot water, and the filtrate and washings are collected in a flask that has a capacity equal to three or four times the volume of the solution. The residue may be fused or discarded, depending on whether it contains iron or not. The practice at this point differs, however. Some chemists prefer to filter every sample, while

others never filter the solution unless the residue contains iron, but simply wash the contents of the beaker into the flask.

In any case, to the solution in the flask add about 10 grams of pure granulated zinc, and place a small funnel in the mouth of the flask. This will catch fine drops of liquid that are carried up with the evolved hydrogen, and will protect the solution from air, while it allows the hydrogen to escape. When the reaction slackens, heat the solution gently to cause as much as possible of the acid to unite with the zinc, forming zinc chloride, which does not interfere with the titration. If a basic-iron salt begins to separate when the acid is nearly all taken up by the zinc, dissolve it in the least necessary quantity of hydrochloric acid, adding the acid drop by drop.

To the solution, which should now contain but a very small amount of free hydrochloric acid, add about 30 cubic centimeters of dilute sulphuric acid, and allow the action of the acid on the zinc to proceed for a few moments, and the iron will all be reduced. It is best, at first, to test the solution by removing a drop of it on a stirring rod, and mixing it with a drop of potassium-sulphocyanide solution previously placed on a spot plate, but after a little experience, this will be unnecessary. Pour the solution through a large fluted filter, and wash the filter by filling it once or twice with pure cold water, receiving the filtrate and washings in a large beaker or porcelain dish. Dilute this solution to 300 or 400 cubic centimeters with cold water, and titrate at once with potassium permanganate.

Many chemists do not filter the solution from the zinc, but add an excess of dilute sulphuric acid, and after the zinc is all dissolved, wash the solution into a beaker or porcelain dish, dilute, and titrate as above. When this is done, there is always danger of small particles of zinc being washed into the dish, and generating hydrogen during titration. As the hydrogen thus generated will reduce some of the permanganate, and thus yield an erroneous result, the writer prefers to filter out the zinc. The results may be obtained more quickly, and, if the filtration is performed as above directed,

the solution is not exposed to the air sufficiently to cause oxidation. By taking up most of the hydrochloric acid with zinc, and titrating the iron in a dilute solution containing considerable free sulphuric acid, the injurious effect of hydrochloric acid is overcome, and the end reaction is as sharp as if no hydrochloric acid were present.

9. The Modified Permanganate Method.—It has been found that by using a so called *titrating mixture* to counteract the evil effects of hydrochloric acid, iron may be reduced with stannous chloride and titrated with permanganate. The chief advantage of this method is the rapidity with which it yields results. Its principal disadvantage is the fact that in the hands of an inexperienced operator, the results may not be accurate, as it requires more skill and experience to make a determination correctly by this method than by either of the methods previously described. As this method is chiefly used where results must be obtained quickly, and as stannous chloride appears to aid in dissolving the ore, a little less of this than the amount required to reduce the iron is usually added at the beginning of the operation, but this is not essential. The process as usually carried out is as follows:

Weigh 1 gram of ore into a small beaker, add about 15 cubic centimeters of concentrate hydrochloric acid and a small amount of stannous chloride (about 5 cubic centimeters for ordinary ores), cover the beaker, and heat on a sand bath or hot plate until the ore is decomposed, but avoid vigorous boiling. If the ore contains organic matter, a little potassium chlorate should be added, and the heating continued until the chlorine and oxide of chlorine are expelled. Wash the cover and sides of the beaker with a jet of water from a wash bottle to bring every particle of iron into the solution, using 15 or 20 cubic centimeters of water for this purpose. Heat this solution nearly to boiling and add stannous chloride from a pipette or burette until the solution becomes colorless, showing that the iron is reduced, but avoiding the addition of more than 2 or 3 drops in excess. It is a good plan to test

this solution, to learn when reduction is complete, by removing a drop of it to a spot plate and mixing it with a drop of potassium sulphocyanide.

When the iron is all reduced, wash the solution into a large beaker or a porcelain dish with cold water, and dilute to about 100 cubic centimeters with cold water. The solution should now be quite cool. Add to it 15 cubic centimeters of mercuric chloride all at once, and stir it vigorously. Then add 50 cubic centimeters of titrating mixture (see Art. 15), and again stir vigorously. Dilute the solution to about 600 cubic centimeters with cold water, and titrate with potassium permanganate as quickly as possible. The end reaction is a faint pink color, which must be noted quickly, as it is of short duration.

SOLUTIONS FOR IRON DETERMINATIONS

10. Standardizing Permanganate and Bichromate Solutions.—The methods of standardizing potassium-permanganate and bichromate solutions by the use of ferrous ammonium sulphate, have been given under Permanganate Method and Bichromate Method, and it is the writer's experience that solutions thus prepared yield accurate results when working on ores, provided a blank determination is made, and the amount of standard solution reduced by reagents, as determined by this blank, is deducted from the reading in each case. Most chemists, however, prefer to standardize solutions against a sample of iron, steel, or ore, the iron contents of which has been carefully determined. Piano wire is largely used for this purpose, but a standard ore has the advantage that standardization and titration are carried on under the same conditions, and in exactly the same manner. The course to be pursued in standardizing a solution for the determination of iron, by any of the methods commonly used, would readily suggest itself from what has been said on this subject under the heading Volumetric Analysis, but in order to make it more clear the method employed when a standard ore is used is given.

Dissolve the potassium permanganate or bichromate in

water, making sure that all is in solution, and then dilute until 1 liter contains, approximately, 6 grams of permanganate or 8.8 grams of bichromate, as the case may be. Mix the solution thoroughly, and, after it has stood for at least 24 hours, standardize it as follows: Dissolve exactly 1 gram of the standard ore, which we will suppose contains exactly 50 per cent. of iron, reduce the solution and titrate with the solution being prepared, following the directions given in Art. 7 for a bichromate solution, or those given in Art. 8 for a permanganate solution. Suppose 49 cubic centimeters of the solution is required to oxidize the iron in the 1-gram sample; then, each 49 cubic centimeters of this solution must be diluted to 50 cubic centimeters in order that 1 cubic centimeter shall oxidize .01 gram of iron. If the volume of the solution amounts to, say, 950 cubic centimeters, the calculation would be: $49 : 50 = 950 : x = 969.4$ cubic centimeters, the required volume, or $969.4 - 950 = 19.4$ cubic centimeters of water must be added. This should not be added all at once, however, for fear of rendering the solution too dilute. It should be diluted nearly to the calculated amount and a second determination made with the standard ore. Then dilute to the exact calculated amount, and check the solution by means of a third determination. It is always best to make duplicate determinations each time when standardizing.

If a standard solution of bichromate is to be made of such strength that 1 cubic centimeter equals .005 gram of iron, it should be diluted until 1 liter contains about 4.4 grams of the pure salt, and .5-gram samples of the standard ore should be used in the determinations. After standardizing the solutions, they should be kept in tightly stoppered bottles in a cool dark place, and should be restandardized every two weeks, as they gradually change in strength owing to slow decomposition or to other causes. It is a good plan to weigh out a sample of the standard ore, and run it with other samples at frequent intervals. Any change in the strength of the solution will thus be detected.

In iron-works laboratories, where many determinations are

made, several liters of the standard solutions are generally made up at a time. The method of preparation is, of course, the same as in the case of smaller quantities. Many chemists do not standardize their solutions so that 1 cubic centimeter oxidizes exactly .01 gram of iron, but make a solution having approximately this strength, and determine the value in iron of 1 cubic centimeter of it. Then, by multiplying the number of cubic centimeters used by the value of 1 cubic centimeter, the amount of iron is obtained, but where many determinations are made, it is an advantage to have the solution of such strength that the percentage of iron may be read directly from the burette.

11. Stannous Chloride.—Different chemists make the stannous-chloride solution, used to reduce the iron, of different strengths, varying from 25 to 150 grams of the dry salt to the liter. A very good solution for this purpose is made by dissolving 80 grams of pure stannous chloride in 500 cubic centimeters of concentrate hydrochloric acid and 500 cubic centimeters of water. The stannous chloride used for this solution should be pure and fresh, for the salt slowly decomposes on standing and forms an insoluble compound. If a pure fresh sample of the salt is not at hand, the solution may be made by dissolving pure metallic tin in concentrate hydrochloric acid and diluting to the proper volume with pure water. If this is done, it is best to place a piece of platinum foil in contact with the tin, to promote solution, which is very slow at best.

12. Mercuric Chloride.—The mercuric-chloride solution, used to oxidize the excess of stannous chloride is generally made by dissolving 50 grams of the salt in 1 liter of water. This makes very nearly a saturated solution, and the reagent is frequently made by adding water to a little more of the salt than it will dissolve, thus keeping a little undissolved salt in the bottle. If this is done, the solution should be shaken up frequently to keep the undissolved salt from forming a hard cake that is not readily dissolved in water.

13. Potassium Sulphocyanide.—The potassium-sulphocyanide solution, used in testing for ferric iron, to learn when reduction is complete, is made by dissolving from 5 to 10 grams of the salt in 100 cubic centimeters of water.

14. Potassium Ferricyanide.—The potassium-ferricyanide solution, used as an indicator in determining iron by the bichromate method, is made by dissolving about .5 gram of the pure solid ferricyanide in 100 cubic centimeters of water. The ferricyanide must be free from ferrocyanide, for this gives a blue color with ferric iron. It may be tested by mixing a drop of it with a drop of ferric solution that is known to be free from ferrous compounds. This solution is slowly reduced by the light, and, consequently, a fresh solution should be made up every day, or at least every second day.

15. Titrating Mixture.—To make the titrating mixture, used when iron is reduced by stannous chloride and titrated with permanganate, dissolve 160 grams of manganoous sulphate in water and dilute the solution to 1,750 cubic centimeters; then add 330 cubic centimeters of 85-per-cent. phosphoric acid, and, finally, stir in 320 cubic centimeters of sulphuric acid of 1.84 Sp. Gr. By using this mixture, iron may be titrated with permanganate in a cold dilute solution containing hydrochloric acid, and satisfactory results obtained, if the titration is performed rapidly.

PHOSPHORUS

16. As the percentage of phosphorus varies greatly in different ores, and as ores differ in solubility, the exact method employed for the determination of this element varies with different ores. Another cause of variation in the details of the method, is the fact that, while, as a rule, exact results are required, it sometimes happens that rapidity is of more importance than extreme accuracy, and in such cases the method is shortened to suit the conditions. As exact results are usually required, a very accurate method

is here described, and if the student should need a more rapid method at any time, he can readily work out a method that will meet his requirements, after studying the determination of phosphorus in iron and steel. In working out a shorter method, the student should remember that the solution from which the ammonium phospho-molybdate is precipitated should have as near as possible the same composition in every case, for the composition of this precipitate varies slightly in different solutions, and if the solution is too strongly acid, the phosphorus will not be completely precipitated; while from an alkaline solution it will not be precipitated at all.

If the ore contains a very high percentage of phosphorus, 1 gram of the sample should be used for this determination, while with ores containing a very low percentage of this

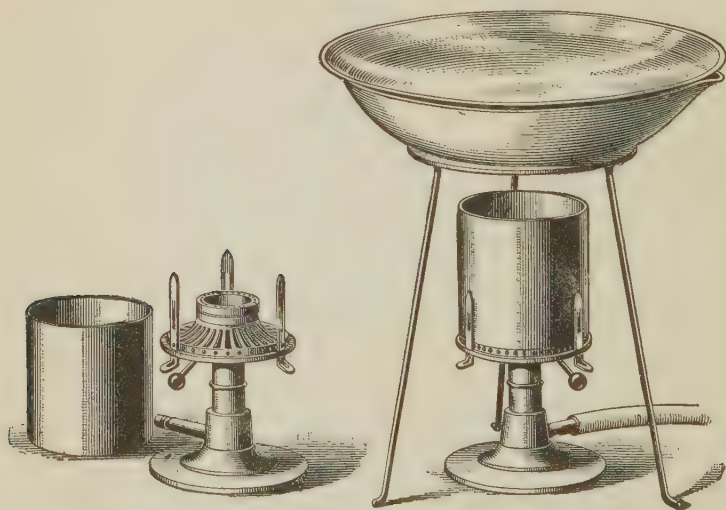


FIG. 4

element, 10 grams are usually taken. The quantity of acid used to dissolve the ore varies with the amount of sample taken, but not in a direct proportion. To dissolve 1 gram of ore, 25 cubic centimeters of acid should be used, while 100 cubic centimeters will be sufficient for 10 grams. This

determination usually proves a stumbling block to the beginner, and, consequently, the directions should be followed as closely as possible until the student becomes familiar with it. After a little practice, however, it becomes very easy to obtain extremely accurate results. The details of the method as used for ordinary ores are as follows:

Weigh 5 grams of the finely powdered sample into a porcelain dish, add 1 cubic centimeter of nitric acid and 75 cubic centimeters of concentrate hydrochloric acid, cover the dish with a watch glass, and digest on a sand bath, a hot plate, or on a tripod placed over an Argand burner, shown in Fig. 4, until the ore appears to be completely decomposed. Then evaporate to dryness, and, to render the silica insoluble, ignite the residue at a moderate temperature until the odor of hydrochloric acid is no longer perceptible. When the residue becomes cool, add 50 cubic centimeters of concentrate hydrochloric acid, heat gently until the mass dissolves, then raise the temperature and boil the solution down to about 20 cubic centimeters. Add 30 cubic centimeters of water, boil for a few moments, filter off the insoluble matter, wash thoroughly with hot water, and stand the filtrate aside. The insoluble residue will seldom contain more than a trace of phosphorus, and, with most ores, in cases where rapidity is of greater importance than extreme accuracy, it may be discarded. As a rule, however, it should be treated as follows:

Place the filter and residue in a platinum crucible and burn off the paper, mix the residue with five or six times its weight of the mixed carbonates of sodium and potassium, and heat till all is in a state of quiet fusion. After cooling, dissolve the fusion in water and hydrochloric acid, and evaporate to dryness in a porcelain dish. Moisten the residue with concentrate hydrochloric acid, again evaporate to dryness, and ignite gently until the odor of hydrochloric acid can no longer be observed. When cool, add from 5 to 10 cubic centimeters of concentrate hydrochloric acid to the residue, heat gently for a few moments, then add 25 cubic centimeters of water, heat to boiling, and filter. Heat the

filtrate to boiling, add a few drops of concentrate nitric acid, and then a slight excess of ammonium hydrate. Any phosphorus that may have remained in the insoluble residue will be carried down in the precipitate thus formed. Filter, wash two or three times with hot water, dissolve the precipitate in the least necessary quantity of hydrochloric acid, and add this solution to the main filtrate, which will now contain all the phosphorus originally in the sample.

Evaporate this solution in a porcelain dish until it becomes syrupy, and the scale of iron oxide that forms on the sides of the dish is only dissolved slowly, but take care not to evaporate the solution until a scale forms that is not dissolved by agitating the solution. Now remove the dish and contents from the flame, immediately add 7 or 8 cubic centimeters of concentrate nitric acid, and, after rotating the dish a few times to mix the solution, wash down the watch glass and sides of the dish with water. Transfer the solution, which must not contain any undissolved matter, to a flask of about 700 cubic centimeters capacity, and wash out the dish, using water enough to bring the volume of the solution up to about 100 cubic centimeters.

To this solution add 30 cubic centimeters of concentrate ammonia, and, after giving the flask a rotary motion to mix the contents, dissolve the precipitate in concentrate nitric acid, adding about 2 cubic centimeters in excess of the amount actually required to give a clear solution. Insert a thermometer in the solution, bring its temperature to exactly 85° , add 75 cubic centimeters of ammonium-molybdate solution, and agitate the mixture for 5 minutes by giving the flask a sharp rotary motion. The phosphorus is thus completely precipitated as ammonium phospho-molybdate, generally known as *yellow precipitate*, which, when precipitated as directed above, contains 1.63 per cent. of phosphorus. Allow the precipitate to settle, which will usually require 15 or 20 minutes, but do not allow it to stand more than 1 hour. Filter and wash the precipitate with water acidified with nitric acid until the iron is completely removed, filling the filter from six to ten times.

The precipitate is next dissolved in ammonia. It is best to dissolve it on the filter and allow the solution to run through into a clean beaker and wash the filter thoroughly. If the silica and iron have been thoroughly removed, as directed above, this is not necessary, however, and the precipitate may be washed into a beaker and dissolved in ammonia. In either case, bring the volume of the solution to about 80 cubic centimeters, add magnesia mixture in considerable excess, and dissolve the precipitate formed in the least necessary quantity of hydrochloric acid. Stand the beaker containing the solution in ice water and slowly add concentrate ammonia while stirring the solution vigorously.

After the solution is rendered alkaline, add about 25 cubic centimeters of concentrate ammonia, stir vigorously and stand aside in a cool place for at least 3 hours for the precipitate to collect and settle. It is a good plan to allow it to stand overnight. Filter, wash the precipitate thoroughly with a dilute solution of ammonia (1 part of concentrate ammonia to 3 parts of water) containing 5 grams of ammonium nitrate in each 100 cubic centimeters of solution, and dry it in an air bath. Remove the precipitate as completely as possible from the filter and burn the latter in a platinum crucible. When cool, add the precipitate, ignite strongly over the blast lamp, cool in a desiccator, and weigh. The precipitate will now generally consist of pure magnesium pyrophosphate $Mg_2P_2O_7$, which contains 27.93 per cent. of phosphorus, but as a little silica may be present, it is best to make a correction as follows:

Fill the crucible to half its capacity with nitric acid of 1.2 Sp. Gr., apply heat until chemical action ceases, and, if an insoluble residue remains, filter it off, wash thoroughly, ignite strongly in a platinum crucible over the blast lamp, and weigh. By deducting this weight from that of the original precipitate, the weight of magnesium pyrophosphate is obtained, and from this the percentage of phosphorus is calculated.

As the percentage of phosphorus in the ammonium phosphomolybdate, precipitated as above directed, is known, this

precipitate may be weighed or titrated by one of the methods described for the determination of phosphorus in iron or steel; but as the gravimetric method in which the phosphorus is finally weighed as magnesium pyrophosphate is the only one that yields exact results in every case, this method should be employed whenever extreme accuracy is required.

SOLUTIONS FOR PHOSPHORUS DETERMINATIONS

17. Ammonium Molybdate Solution.—There are many formulas for making this solution, and several of these that the writer has tried have proved very satisfactory. The following formula is a very good one, where large quantities of the solution are used. If the student wishes to make up a smaller amount of the solution, he can use smaller quantities of the constituents, keeping the proportion the same, of course.

Mix 700 cubic centimeters of ammonia (Sp. Gr. .90) with 1,325 cubic centimeters of water. Dissolve in this 500 grams of molybdic anhydride MoO_3 . Mix 2,415 cubic centimeters of nitric acid (Sp. Gr. 1.42) with 4,090 cubic centimeters of water. Allow the two solutions to cool, and if any impurities remain undissolved, filter the molybdate solution. When both solutions are cool, pour the molybdated solution slowly into the nitric acid, stirring constantly. Do not pour the nitric acid into the molybdate. In laboratories having an air blast, the agitation may be accomplished by passing a current of air through the solution. When all is added, stand the solution in a warm place for 24 hours, and decant the clear solution, or filter before using. When this solution is to be used for the volumetric determination of P_2O_5 , 5 cubic centimeters of strong nitric acid should be added to each 100 cubic centimeters and the solution filtered before using.

18. Magnesia Mixture.—The magnesia mixture for this purpose is frequently made as follows: Dissolve 110 grams of pure crystallized magnesium chloride and 280 grams of ammonium chloride in 1,300 cubic centimeters of

water. To this add 700 cubic centimeters of ammonia of .96 Sp. Gr., shake well, allow to stand several days, and filter before using.

19. Nitric-Acid Wash.—To make the dilute nitric acid used in washing the “yellow precipitate,” measure 15 or 20 cubic centimeters of concentrate nitric acid (Sp. Gr. 1.42) into a wash bottle, fill up to 1 liter with pure water and shake well. The solution is generally made to contain 20 cubic centimeters of nitric acid to the liter, but some chemists prefer a more dilute solution.

SULPHUR

20. Sulphur occurs in iron ores both in the form of sulphides and sulphates. It must all be obtained in the form of a soluble sulphate, and precipitated as barium sulphate by means of barium chloride. In the case of most ores, the sulphur may be obtained in the form of a soluble sulphate, either by treating the ore with hydrochloric and fuming nitric acids, or by fusing it with the mixed carbonates of sodium and potassium and potassium nitrate. The fusion method is the only one that yields accurate results in all cases, but as the treatment with acids is the handiest in cases where it is admissible, both methods are given.

21. The Aqua-Regia Method.—Weigh 5 grams of the ore into a rather deep porcelain dish, cover it with a watch glass, and slowly add 20 cubic centimeters of fuming nitric acid. When the action nearly ceases, add 30 cubic centimeters of concentrate hydrochloric acid, and allow it to stand at the temperature of the laboratory for a short time—an hour or two, if time permits. Transfer to a water bath or a sand bath, and digest at a gentle heat until the ore appears to be decomposed. Then add 1 gram of sodium carbonate dissolved in 10 cubic centimeters of water, raise the temperature, and evaporate to dryness. In order to render the silica insoluble, moisten the residue with concentrate hydrochloric acid,

again evaporate to dryness, and ignite gently until the odor of hydrochloric acid is no longer given off.

When cool, add 10 cubic centimeters of concentrate hydrochloric acid, heat for a few moments, then add 50 cubic centimeters of water and boil till solution is complete. Filter off the insoluble matter, and wash with hot water until the soluble material is completely removed from the paper, and the volume of the solution amounts to from 150 to 200 cubic centimeters. Heat the solution to boiling, add a moderate excess of barium chloride (25 cubic centimeters of a 5-per-cent. solution is sufficient for most ores), and continue the boiling for several minutes. Stand the solution on a water bath or other warm place for an hour, then stand it in a cool place till the precipitate has completely settled and the solution is cool.

Filter, preferably, through a Gooch crucible. When the solution has run through, fill it up with hot water, and when this has run through, wash once with hot dilute hydrochloric acid, and then wash thoroughly with hot water. Suck the water out of the asbestos as completely as possible, dry, and ignite it at a dull-red heat for 5 minutes, cool in a desiccator, and weigh as barium sulphate $BaSO_4$, which contains 13.73 per cent. of sulphur. If a filter paper is used instead of a Gooch crucible, the precipitate should be removed from it as completely as possible, and the paper burned cautiously before the precipitate is ignited.

22. The Fusion Method.—Mix 1 gram of the pulverized ore with about 6 grams of sodium and potassium carbonates, and .5 gram of potassium nitrate; introduce this mixture into a large platinum crucible and cover it with a mixture of about 2 grams of the mixed carbonates, and .25 gram of potassium nitrate. Cover the crucible and heat it at a gradually increasing temperature until the mass is in a state of quiet fusion, but do not ignite longer than necessary, as this mixture is likely to injure the crucible if the heating is continued too long. Run the fusion well up on the sides of the crucible and cool it rapidly by dipping it in

cold water, taking care not to let any water get inside of the crucible. When cool, place the crucible and contents in a porcelain dish, add about 100 cubic centimeters of water, and boil to dissolve the fused mass. When the fusion is loosened from the crucible, remove it, and wash it off into the dish by means of a wash bottle. If any hard lumps remain in the solution, they may be broken up by gently rubbing with a pestle, which must afterwards be washed off into the dish.

When the fusion is completely disintegrated, allow the undissolved portion of iron, etc. to settle, and, if the solution has a green or red tint, add a few drops of alcohol to precipitate the manganese, which causes this color. Filter, and wash the precipitate thoroughly with hot water, collecting the filtrate and washings in a porcelain dish. Render the filtrate distinctly acid by the cautious addition of concentrate hydrochloric acid, evaporate to dryness, and ignite gently to render the silica insoluble. Moisten the residue with 5 cubic centimeters of concentrate hydrochloric acid, add from 50 to 75 cubic centimeters of water, and heat until the sodium salts are completely dissolved. Filter, and wash thoroughly with hot water, bringing the volume of the filtrate to about 150 cubic centimeters. Heat this filtrate to boiling, add 10 cubic centimeters of a 10-per-cent. solution of barium chloride (or 20 cubic centimeters of a 5-per-cent. solution), and continue the boiling for several minutes.

Stand the solution in a warm place for from 4 to 6 hours for the precipitate to collect and settle in a coarse granular form, filter, wash thoroughly with hot water, and dry in an air bath. Remove the precipitate as completely as possible from the filter and burn the latter in a weighed crucible. Moisten the ash with a drop of nitric and a drop of sulphuric acid, heat gently at first, and then raise the temperature to faint redness to drive off the excess of acid. Add the precipitate, heat to dull redness for 5 minutes, cool in a desiccator, and weigh as barium sulphate $BaSO_4$, which contains 13.73 per cent. of sulphur.

If preferred, the barium sulphate may be filtered on a Gooch felt, but, when this method is employed, the precipitate

is generally obtained in a form so coarse that it does not run through a filter, and, consequently, the use of a Gooch crucible is not necessary. It is frequently advised to heat the barium chloride, used to precipitate the sulphur, to boiling before adding it, in order to obtain the precipitate in a coarser form; but if the boiling is continued for some minutes after the addition of the barium chloride, this is unnecessary.

MANGANESE

23. More or less manganese is found in nearly all iron ores, and its determination is often a matter of importance. The two methods that are probably the most used are Volhard's method and Ford's method. Both these methods have been more or less modified by different chemists, and they are given here, not exactly as they were originally described by their authors, but as they are most frequently used in practical work.

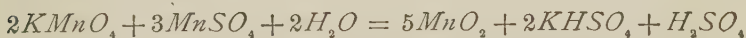
Volhard's method is quite rapid and simple, and it is the writer's experience that it yields accurate results in all cases. Many chemists, however, do not consider it accurate for ores containing less than .5 per cent. of manganese, and Ford's method is generally considered the more reliable of the two. Hence, although it is longer, Ford's method is generally used when exact results are required, especially if the ore contains but little manganese. Both these methods may be used for manganese ores as well as for the ores of iron.

24. Volhard's Method.—Weigh 1.5 grams of the sample into a porcelain dish, add 20 cubic centimeters of concentrate hydrochloric acid, about 10 drops of concentrate nitric acid, and 15 cubic centimeters of dilute sulphuric acid (1 part of acid of 1.84 Sp. Gr. to 2 parts of water). Evaporate to dryness on a hot plate, and ignite till dense white fumes of sulphur trioxide are given off. When cool, add about 75 cubic centimeters of water, and boil until the sulphates are completely dissolved. Wash the solution into a 300-cubic-centimeter graduated flask, cool the solution, add a strong solution

of sodium carbonate until the solution is almost neutral and assumes a red color, but no precipitate forms; then add an emulsion of zinc oxide in water until the color becomes light brown, generally described as the color of coffee with cream.

Dilute exactly to the mark with pure water, and mix thoroughly. Pour this mixture on a large, dry, fluted filter, placed in a dry funnel, and receive the filtrate in a dry clean beaker. By means of a pipette, transfer 200 cubic centimeters of this filtrate, which represents 1 gram of ore, to a flask, and heat it to boiling. As soon as the solution commences to boil, remove it from the source of heat, run in a little standard potassium-permanganate solution, give the flask a sharp rotary motion to cause the precipitate to collect, allow it to partly settle and note the color of the solution. If the solution is colorless, add more permanganate, shake the flask, allow the precipitate to partially subside, note the color of the solution, and continue this treatment until the supernatant liquid shows a pink color after the precipitate has settled. This titration must be rapidly performed, so as to allow little time for the solution to cool.

When a potassium-permanganate solution is added to a solution of manganese sulphate at about the boiling point, the manganese in both solutions is precipitated according to the equation:



When all the manganese in the manganese-sulphate solution is precipitated, the excess of permanganate added gives the solution a pink tint, which indicates the end of the reaction. Knowing the strength of the permanganate solution, the amount of manganese in the sample is readily calculated from the above equation. If the ore contains a very high percentage of manganese, it is best to dilute the 200 cubic centimeters of solution, withdrawn after filtering, to some exact volume, depending on the amount of manganese present; and then take 200 cubic centimeters of this solution for titration.

25. Ford's Method.—Weigh 1 gram of ore into a porcelain dish, add 25 cubic centimeters of concentrate hydrochloric acid and evaporate to complete dryness, but avoid a temperature much above 100°. Add 5 cubic centimeters of concentrate hydrochloric acid and 20 cubic centimeters of water to the residue, and boil till the chlorides are all in solution.

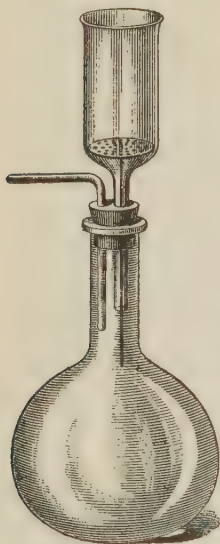


FIG. 5

Filter off the silica, wash it thoroughly with hot water, and evaporate the filtrate to dryness, but avoid ignition. Dissolve the residue in concentrate nitric acid, and boil the solution down until it is almost syrupy, to expel hydrochloric acid. Add 50 cubic centimeters of concentrate nitric acid, boil for a few minutes, and then add, a little at a time, from 5 to 8 grams of potassium chlorate to oxidize the manganese and precipitate it as manganese dioxide MnO_2 . When enough has been added to oxidize the manganese, the greenish-yellow vapors above the solution will give a puff and disappear. Now add about 1 gram more of potassium chlorate and boil about 2 minutes; then cool rapidly by standing the beaker in cold water, and, when it is

cold and the precipitate has settled, filter through an asbestos filter.

To make a filter for this purpose, a perforated porcelain disk, such as is used with a porcelain Gooch crucible, is attached to a stout platinum wire and placed in a filtering tube fitted in a filtering flask, as shown in Fig. 5. Pour the asbestos suspended in water into the tube, and, by means of the pump, draw the water through, depositing the asbestos on the disk, forming a filter, or "plug," as it is generally called. If a disk and wire for this purpose are not at hand, an irregular piece of glass, or a piece of pumice stone, may be placed in the neck of the filtering tube, and the asbestos deposited on it.

Wash the beaker and precipitate twice with concentrate nitric acid by pouring 15 or 20 cubic centimeters of it into the beaker in which the precipitation was accomplished, and, after running it around in the beaker, pour it on the precipitate and draw it through the plug. When all has passed through the filter, repeat the operation. The acid used for washing the precipitate must be pure and colorless; if it is colored by nitrous fumes, which are always developed in nitric acid that is allowed to stand in the light, it will dissolve the manganese dioxide; but acid thus colored may be purified by passing a current of air through it.

By pressing on the end of the platinum wire extending through the bottom of the filtering tube, force the precipitate and asbestos out into the beaker in which the precipitation was made; or, if a platinum wire were not used, the precipitate and plug may be forced out by means of a thin stirring rod. Add about 30 cubic centimeters of strong sulphurous acid (made by leading sulphur dioxide into water) and 5 cubic centimeters of hydrochloric acid, pouring the acids through the filtering tube to dissolve any precipitate that may be adhering to it. Stir the precipitate and asbestos up with a glass rod, and the acid mixture will rapidly dissolve the manganese dioxide. Filter to remove the asbestos, and wash it well on the filter with hot water. Boil the filtrate until the excess of sulphur dioxide is driven off, add a few drops of concentrate nitric acid, and, after boiling a few moments longer, add a slight excess of ammonium hydrate to precipitate the iron present. Filter, wash several times with hot water, and stand the filtrate aside. Dissolve the precipitate on the filter with hydrochloric acid, allow the solution to run through and wash the filter well with hot water, receiving the solution and washings in a clean beaker. Heat the solution to boiling, reprecipitate the iron with ammonia, filter, and wash the precipitate thoroughly with hot water.

Unite the two filtrates, which will now contain all the manganese freed from other metals, and the volume of which should amount to about 300 cubic centimeters. Add a rather

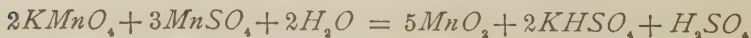
large excess of microcosmic-salt solution (from 20 to 50 cubic centimeters, according to the amount of manganese present) and dissolve the precipitate thus formed in the least necessary quantity of concentrate hydrochloric acid. Heat the solution to boiling, and, while keeping it as near as possible to the boiling point, add concentrate ammonia, drop by drop, until the last drop causes a permanent precipitate. Now stop the addition of ammonia, and stir the solution vigorously until the precipitate assumes a silky crystalline appearance; then add another drop or two, stir again, and continue this treatment until the manganese is all precipitated in the crystalline condition. Then add 2 or 3 cubic centimeters of the ammonia in excess, and stir well. Stand the beaker in a cool place until the solution is cool and the precipitate has completely settled.

It may be filtered after standing 20 minutes, but if there is no hurry, it is best to allow it to stand 2 hours. Filter and wash thoroughly, but not excessively, with water made slightly alkaline with ammonia, and containing 100 grams of ammonium nitrate to the liter. Dry in an air bath, remove the precipitate as completely as possible from the filter, and burn the latter in a weighed crucible. Add the precipitate, ignite intensely over the blast lamp, cool in a desiccator, and weigh as manganese pyrophosphate $Mn_2P_2O_7$, which contains 38.73 per cent. of manganese.

SOLUTIONS FOR MANGANESE DETERMINATIONS

26. Zinc Oxide.—The zinc-oxide emulsion, used to precipitate the iron in Volhard's method, is prepared by mixing pure zinc oxide with water until it has a creamy consistency. The zinc oxide separates out on standing, and, consequently, it must be shaken thoroughly before it is used.

27. Potassium Permanganate.—The standard permanganate solution, used in titrating iron, may be used for this determination by making a calculation. The manganese is precipitated according to the equation:



Hence we see that 2 molecules of permanganate, which oxidize 10 molecules of ferrous sulphate, only oxidize 3 molecules of manganese sulphate. Taking the atomic weights of iron and manganese as 56 and 55, respectively, we have $\frac{55}{56} \times \frac{3}{10} = \frac{33}{112}$, or .2946. That is, the value of the permanganate solution in iron, multiplied by .2946, gives its value in manganese, or the value of a permanganate solution in manganese is 29.46 per cent. of its value in iron.

It is best, however, if many determinations are to be made, to make, for this purpose, a solution of permanganate of such strength that the percentage of manganese may be read directly from the burette, and this plan is universally adopted in iron-works laboratories where this method is used. If the solution titrated represents one gram of ore, the permanganate solution should be made of such strength that 1 cubic centimeter of it oxidizes .001 gram of manganese, corresponding to .1 per cent. The method of standardizing will be readily understood from the above calculation.

PIG IRON

28. As pig, or cast, iron is the first product in the manufacture of iron and steel, its analysis will be treated next. The principal determinations, and, in fact, the only determinations frequently made, are four in number; viz., *silicon*, *sulphur*, *phosphorus*, and *manganese*. As all these elements tend to segregate to a greater or less extent, pig iron is never homogeneous; a single pig will not have exactly the same composition throughout, and, if samples are taken from different parts of a cast, the variation will be still greater; hence the selection of a sample becomes a matter of importance. If a cast is to be sampled, probably the best method is to remove three samples of the molten iron, as it runs from the furnace, by means of a ladle, taking the first sample soon after the iron begins to run, the second when about half of it has passed out, and the third towards the end of the cast. After these test pieces have cooled, break them, drill an equal amount from the interior of each piece, and mix the drillings.

A sample is thus obtained that, as a rule, quite closely represents the composition of the whole cast.

If a car of metal is to be sampled, pigs should be taken from different parts of the car, then broken, and mixed with the same quantity of drillings taken from the interior of each pig. This method should also be employed in sampling a pile of iron.

Iron drillings are always likely to contain sand and scale, and these must be removed before weighing up a sample. This is best done as follows: Spread the drillings on a clean paper, place another paper over them and bring a magnet in

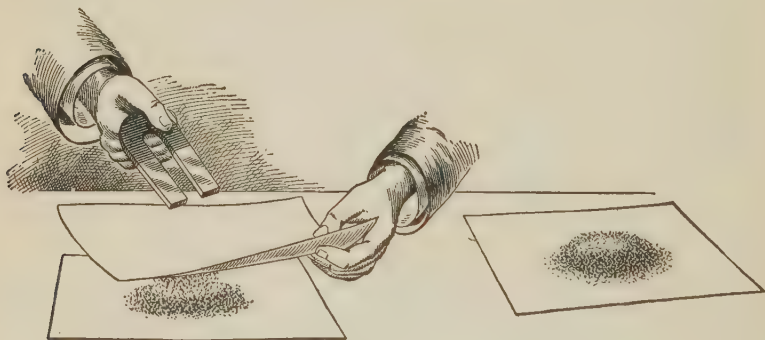


FIG. 6

contact with this paper. By lifting up on the magnet, which attracts the drillings and holds them close to the paper, remove part of the drillings and hold them over another clean paper. Then by holding the paper between the magnet and drillings firmly, and withdrawing the magnet, allow the drillings to fall on the paper placed to receive them. By repeating this a few times, all the drillings will be removed to the second paper, while the sand and scale, being non-magnetic, will remain on the first. The method of accomplishing this is illustrated in Fig. 6. Now, after mixing the sample thoroughly to get a uniform mixture of coarse and fine drillings, which usually differ somewhat in composition, the sample is ready to be weighed out for the different determinations.

It should be mentioned at this point that a short piece of thick iron wire, ground to a point and magnetized, is very handy in transferring small particles of the sample to and from the weighing glass on the pan of the balance.

SILICON

29. Drown's Method.—For this determination, the method proposed by Dr. Drown, or a slight modification of the same, is almost universally adopted. The method, as it is probably most frequently employed, is as follows: Weigh 1 gram of drillings into a porcelain dish, cover the dish with a watch glass, and add 20 cubic centimeters of nitric acid of 1.2 Sp. Gr., drawing the glass aside to admit the acid. If the drillings are very fine, the acid should be added cautiously to prevent loss during solution. When violent action ceases, add 15 cubic centimeters of dilute sulphuric acid (1 part of acid to 2 parts of water), evaporate to dryness on a hot plate, or over the bare flame of an Argand burner, and continue to heat until copious white fumes of sulphur trioxide are given off.

If the heat is carefully regulated, the evaporation may be accomplished without spattering, but as there is always more or less danger, it is best to keep the dish covered with a watch glass to catch any particles that may spatter against it, and would otherwise be lost, and to boil the solution down rapidly. When cool, add 15 cubic centimeters of dilute hydrochloric acid (equal parts of acid and water, generally spoken of as 1 : 1 acid), then from 30 to 50 cubic centimeters of water, and boil vigorously until the sulphates are completely dissolved. Wash any precipitate adhering to the watch glass into the solution, and, after allowing it to stand a few moments for the precipitate to settle, filter while still quite warm, preferably with the aid of a filter pump. Wash twice with hot water, then fill the filter with warm dilute hydrochloric acid (generally 1 : 1), and when this has passed through, continue to wash with hot water until the iron is completely removed from the precipitate

and filter. The precipitate now consists of silica and graphite. Wrap the filter around it, place them in a platinum crucible, and, after igniting moderately to burn the paper, heat at the full power of the blast lamp until the graphite is burned off, leaving the precipitate perfectly white. When cool, weigh as silica SiO_2 , which contains 47.02 per cent. of silicon.

The results obtained as just directed are accurate enough for all practical purposes, but, if absolute accuracy is required, add 2 or 3 drops of sulphuric acid to the silica after weighing it; then dissolve it in hydrofluoric acid, evaporate to dryness, ignite, cool, and weigh the residue, if any, remaining in the crucible. The difference between the two weights is the weight of silica which has been expelled by heating the hydrofluoric-acid solution. When many determinations are made daily, this method is frequently modified as follows: Weigh .9404 gram of the sample into a porcelain dish, dissolve it in 25 cubic centimeters of mixed acids (made up in the proportion of 18 parts of nitric acid of 1.2 Sp. Gr. to 7 parts of half-strength sulphuric acid), evaporate to dryness, and heat until dense white fumes of sulphur trioxide

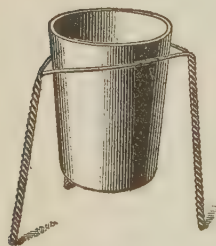


FIG. 7

are given off. When cool, dissolve the sulphates in hydrochloric acid and water, filter, wash, ignite (usually in a muffle furnace), and weigh. As .9404 is twice the factor weight (.4702) of silicon, the weight of silica divided by 2 is the percentage of silicon. When precipitates are ignited in a muffle furnace, they are usually placed, together with the filter, in a platinum crucible that is supported on a

tripod of platinum wire, as shown in Fig. 7. The crucible standing in the tripod is placed in a muffle maintained at a white heat until the precipitate is white, then it is removed and is weighed as soon as cool. As twenty-five or thirty precipitates may be ignited at one time in a muffle, much time is saved by this method of ignition if many determinations are being made.

SULPHUR

30. A number of methods for the determination of sulphur in iron have been proposed, but only two, known as the *evolution method* and the *aqua-regia method*, are used very extensively in iron-works laboratories. The evolution method depends on the fact that all the sulphur in iron exists in the form of sulphide, and can ordinarily be evolved in the form of hydrogen sulphide by treating the sample with hydrochloric acid. By the aqua-regia method, the sulphur is oxidized to sulphate, and is precipitated and weighed as barium sulphate.

The evolution method is rapid and simple, and with most samples yields extremely accurate results. Occasionally, however, a sample is met that will not yield all its sulphur by this method; hence, in settling disputes, and in establishing standards, the aqua-regia method should always be employed.

31. The Evolution Method.—Weigh 5 grams of drillings into a flask having a capacity of 750 or 800 cubic centimeters, and close the flask with a doubly perforated stopper. Through one of the perforations of this stopper pass a funnel tube with a stop-cock, reaching nearly to the bottom of the flask, and, through the other, pass a short delivery tube bent at right angles, over the end of which a short piece of rubber tubing is tightly fitted. Place a tight-fitting, doubly perforated rubber stopper in a test tube containing an ammoniacal solution of cadmium chloride, and through one perforation pass a glass tube reaching nearly to the bottom of the test tube, and connect this with the rubber tube attached to the delivery tube of the flask. Through the other perforation pass the short limb of a tube bent twice at right angles, so that it reaches just through the stopper, and pass the longer limb nearly to the bottom of a second test tube, fitted like the first. Each tube should contain 25 cubic centimeters of cadmium-chloride solution and 25 cubic centimeters of water. Fit the flask in a suitable support over an Argand burner. The test tubes may be supported by the tube connecting them.

The arrangement of the apparatus will be understood from Fig. 8. Close the apparatus, and pour from 90 to 100 cubic centimeters of hydrochloric acid (1 : 1) into the funnel tube. Then turn the stop-cock, allowing the acid to run into the

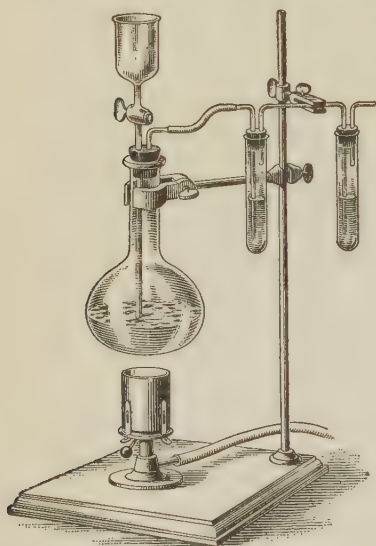


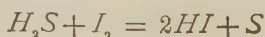
FIG. 8

flask, and, as soon as it is all in, close it again. The iron is rapidly dissolved with the evolution of hydrogen, and the sulphur, which is in the form of sulphide, is evolved as hydrogen sulphide. The gases pass through the test tubes containing cadmium chloride where the hydrogen sulphide is absorbed with the formation of cadmium sulphide.

When the evolution of gas slackens, light the burner under the flask, and turn it low until the iron is all dissolved; then raise the temperature and boil the solution

until all hydrogen sulphide is expelled and the solution in the first test tube is quite warm from the steam passing over from the flask. Now open the stop-cock of the funnel tube, turn out the light, and disconnect the rubber tube connecting the flask and test tubes. Remove the test tubes, pour their contents into a beaker, and thoroughly wash the test tubes and tubes leading into them, allowing the washings to run into the solution in the beaker, which is then diluted to about 300 cubic centimeters. Add about 5 cubic centimeters of starch solution, render the solution distinctly acid with hydrochloric acid, and titrate at once with a standard solution of iodine.

When the solution is rendered acid with hydrochloric acid, hydrogen sulphide is formed, and this reacts with the iodine according to the equation:



This reaction takes place as long as the solution contains hydrogen sulphide, but as soon as this is consumed, the iodine commences to unite with the starch, forming blue starch iodine; hence the appearance of a permanent blue color indicates the end of the reaction. The solution must be titrated immediately after it is acidified, or the hydrogen sulphide formed will partly escape, and the results obtained will be too low. For the same reason, the acid used to acidify the solution should be added quickly.

In iron-works laboratories, a series of supports is generally arranged over stationary Argand burners, which are much better than Bunsen burners for this purpose; but for practice, or for an occasional determination, the apparatus shown in Fig. 8 serves very well, and in such cases a Bunsen burner or even an alcohol lamp may be substituted for the Argand burner.

32. The Aqua-Regia Method.—Weigh 5 grams of drillings into a porcelain dish, or, still better, a porcelain beaker, and quickly add 50 cubic centimeters of nitric acid of 1.42 Sp. Gr., so that the sample is completely covered at once. If rapid solution commences at once, stand the porcelain dish in cold water to check the action. If the sample does not begin to dissolve in a few moments, add a few drops of concentrate hydrochloric acid, and heat it gently. Violent action may be checked by standing the dish in cold water, preferably, ice water.

About 10 cubic centimeters of hydrochloric acid should be added in small portions during the solution. When this is all in, and the sample is dissolved, add about $\frac{1}{2}$ gram of potassium chlorate and 1 gram of sodium carbonate, evaporate to dryness, and ignite slightly. Dissolve the residue in 20 or 25 cubic centimeters of concentrate hydrochloric acid, evaporate to dryness, and again ignite gently to render the silica insoluble. Dissolve the residue in 25 or 30 cubic centimeters of concentrate hydrochloric acid, and evaporate until the solution becomes syrupy; then add 5 cubic centimeters more of concentrate hydrochloric acid, and heat

gently till the solution becomes clear. Dilute this solution with a little more than twice its own volume of hot water, mix thoroughly, filter through a paper that has previously been washed with hot dilute hydrochloric acid, and wash the filter thoroughly with hot water, adding a few drops of hydrochloric acid, if necessary, to remove red stains from the paper.

Heat the filtrate, which should amount to about 200 cubic centimeters, to boiling, add 20 cubic centimeters of a 5-per-cent. solution of barium chloride, or 10 cubic centimeters of a 10-per-cent. solution, and continue the boiling a few minutes. Stand the solution in a warm place for at least 2 hours; then filter, and wash thoroughly on the filter with hot water, acidulated with a few drops of hydrochloric acid. Dry the precipitate in an air bath, remove it as completely as possible from the filter, and burn the latter in a weighed crucible. Add 1 or 2 drops each of concentrate nitric and sulphuric acids, evaporate to dryness, and ignite gently to expel the excess of acid. When cool, add the precipitate, heat to dull redness, cool in a desiccator, and weigh as barium sulphate $BaSO_4$, which contains 13.73 per cent. of sulphur.

A Gooch crucible may be used instead of a filter paper in filtering the barium sulphate, and is preferred by many chemists on account of the tendency of the precipitate to pass through a filter, and the ease with which it is reduced when ignited in the presence of carbonaceous matter.

In the case of some samples of iron containing a high percentage of sulphur, a small quantity of this element appears to escape oxidation when the sample is dissolved as above directed. In such cases, it is best to stand the dish containing the sample in cold water, add the nitric acid quickly so that the drillings are entirely covered at once, and allow the dish to stand in the cold water about an hour. Then add 10 cubic centimeters of concentrate hydrochloric acid, and allow the dish to stand in a cool place several hours longer before applying heat to effect solution. In this way, much of the sulphur is oxidized before there is

any apparent action, and the results obtained are slightly higher, in some cases, than when the sample is dissolved in the usual manner.

SOLUTIONS FOR SULPHUR DETERMINATIONS

33. Cadmium-Chloride Solution.—This solution is made up as follows: Dissolve 100 grams of cadmium chloride in 500 cubic centimeters of water and 500 cubic centimeters of concentrate ammonia, and filter through a fluted filter into a large bottle. To the filtrate add 2 liters of concentrate ammonia and 2 liters of water, and mix thoroughly. Generally for the absorption, a single test tube 1 inch in diameter and 10 or 12 inches in length, with a delivery tube reaching to the bottom, is used. About 25 cubic centimeters of the cadmium solution, diluted to about 100 cubic centimeters, are introduced into the tube, and the determination proceeded with as directed. It is safer, however to divide this solution between two test tubes, as directed.

Instead of the cadmium solution one of zinc may be used. This may be prepared by dissolving 70 grams of zinc oxide in hydrochloric acid, using only enough hydrochloric acid to decompose the oxide. Add 500 cubic centimeters of concentrate ammonia, and filter if necessary. Add 2 liters of strong ammonia and 2 liters of water; mix thoroughly. This solution is used in the same way as the cadmium solution, and has been found equally as satisfactory.

Some chemists use a solution of potassium hydrate to absorb the H_2S . A good strength of this solution is got by dissolving 200 grams KOH in water and diluting to 1,000 cubic centimeters. When using this solution the amount of hydrochloric acid required to render acid the amount of KOH solution used should be determined, and this amount of acid added before titrating. With the cadmium and zinc solutions, the disappearance of the odor of ammonia shows that the solution is acid; but with the potash solution it is best to measure the acid.

34. Starch Solution.—To make the starch solution for the indicator, mix from 5 to 10 grams of pure starch with

40 or 50 cubic centimeters of water; pour this into a liter of boiling water, and continue the boiling a few moments, meanwhile stirring with a glass rod. Allow the solution to settle, and decant the clear liquid for use. A fresh solution should be made up at least once a week.

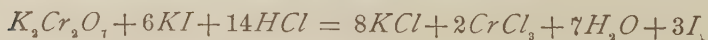
35. Standard Iodine Solution.—The iodine solution is made of such strength that 1 cubic centimeter represents .0005 gram of sulphur, or .01 per cent. of sulphur when 5 grams of sample are taken. The reaction between hydrogen sulphide and iodine is



or 254 grams of iodine set free 32 grams of sulphur. Hence, in order that 1 cubic centimeter of the solution shall represent .0005 gram of sulphur, 1 liter of it must contain 3.969 grams of iodine.

It is common practice to standardize the iodine solution against a steel of known sulphur content. This is done as follows: Dissolve 10 or 12 grams of potassium iodide in from 50 to 75 cubic centimeters of cold water, add 4 grams of freshly sublimed iodine, stir till all is dissolved, and dilute to about 1 liter. Then dissolve 5 grams of the standard steel in half-strength hydrochloric acid, absorb the hydrogen sulphide in cadmium chloride, as directed in Art. 31, and titrate with this solution. From the result thus obtained, calculate how much the solution must be diluted, add the calculated amount of water and mix thoroughly. Then make another determination, using the standard steel, to be sure that the solution is right. This solution should be kept in a dark, cool place and should be restandardized once a week.

As potassium bichromate liberates iodine from its compounds, an iodine solution may be made up and standardized at the same time by the use of a standard solution of potassium bichromate. The reaction is as follows:

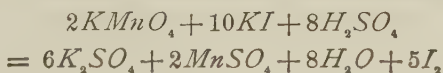


Hence, 1 cubic centimeter of a decinormal solution of

potassium bichromate, which oxidizes .0056 gram of iron, liberates .0127 gram of iodine, and 312.5 cubic centimeters liberate 3.969 grams of iodine. The solution is made up as follows:

Dissolve about 15 grams of potassium iodide in 200 cubic centimeters of water. Then dilute 10 cubic centimeters of concentrate hydrochloric acid to 200 cubic centimeters, add this to the potassium-iodide solution, and, from a burette, run in 312.5 cubic centimeters of decinormal bichromate solution while stirring continuously. Dilute this solution to exactly 1 liter and mix it thoroughly, when it will be ready for use.

The same volume of a decinormal solution of potassium permanganate may be used instead of the bichromate by substituting sulphuric for hydrochloric acid. If this is done, pour 10 cubic centimeters of concentrate sulphuric acid into 200 cubic centimeters of water, and, after this solution has cooled, slowly pour it into the potassium-iodide solution while stirring continuously. Add 312.5 cubic centimeters of decinormal permanganate solution to this, and proceed as with the bichromate. The reaction in this case is as follows:



PHOSPHORUS

36. A number of methods for the determination of phosphorus in pig iron are in general use. In most of these methods, the phosphorus is first precipitated as ammonium phospho-molybdate, generally spoken of as "yellow precipitate," and the various methods differ principally in the treatment of the yellow precipitate.

37. Obtaining the Yellow Precipitate.—Weigh 5 grams of the drillings into a porcelain dish, cover with a watch glass, and add 70 cubic centimeters of nitric acid of 1.2 Sp. Gr. When violent action ceases, place the dish on a tripod over an Argand burner, which is turned very low

until solution is complete. This will usually require about half an hour. Now raise the temperature, evaporating to dryness as rapidly as possible, and ignite the residue until acid fumes are no longer given off. The carbonaceous matter is thus destroyed, and the phosphorus is oxidized to phosphate. When cool, add 35 cubic centimeters of concentrate hydrochloric acid and heat gently till the residue is dissolved; then raise the temperature, and evaporate as rapidly as possible, with the cover on, until the solution becomes syrupy, thus expelling as much hydrochloric acid as possible without having iron salts separate.

Remove the dish from the burner, add 20 cubic centimeters of concentrate nitric acid, boil down to about 8 cubic centimeters, this should drive off the rest of the chlorine; then, without delay, wash any iron solution adhering to the watch glass and the sides of the dish down into the main solution, using from 75 to 100 cubic centimeters of warm water, and stir the solution well. Filter into a flask having a capacity of about 700 cubic centimeters, and wash the filter and residue thoroughly with a 2-per-cent. solution of nitric acid. To the solution in the flask add 30 cubic centimeters of concentrate ammonia, shake the flask until the precipitate becomes smooth, then add enough concentrate nitric acid to dissolve it, forming a clear amber-colored solution.

Suspend a thermometer in the solution, bring its temperature to exactly 85° , add 75 cubic centimeters of ammonium molybdate, and agitate the contents of the flask for 5 minutes by giving the flask a rotary motion, or by shaking it. The phosphorus will now be completely precipitated as ammonium phospho-molybdate. After allowing it to settle for 15 or 20 minutes, filter and determine the phosphorus in it by one of the following methods.

38. Weighing as Magnesium Pyrophosphate.—Wash the yellow precipitate thoroughly with 2-per-cent. nitric acid, dissolve it in ammonia, precipitate the phosphorus as magnesium-ammonium phosphate, ignite strongly, and weigh as

magnesium pyrophosphate, following the directions given in Art. 16.

This method is much longer than some of the others, but, as it is probably the most reliable of any, it is largely used in settling disputes, and in other cases where extreme accuracy is required.

39. Titration With Permanganate.—Wash the precipitate thoroughly with an acid ammonium-sulphate solution, place the funnel in the neck of a 500-cubic-centimeter flask, spread the filter on the side of the funnel, or break its apex with a glass rod, and wash as much of the precipitate as convenient into the flask with water. To dissolve the precipitate adhering to the paper, pour dilute ammonia over it, and wash the paper thoroughly with water, allowing all the solution to run into the flask.

Enough ammonia should be added to dissolve all the yellow precipitate, both on the filter and in the flask, but a large excess should be avoided. Pour 15 grams of granulated zinc into the flask, add 100 cubic centimeters of dilute sulphuric acid (made by adding 1 part of concentrate acid to 3 parts of water), place a small funnel in the neck of the flask and heat gently for half an hour, when reduction will be complete.

Pour the contents of the flask, which should still contain some undissolved zinc, upon a large folded filter, receiving the filtrate in a large beaker. Rinse out the flask with water, and, as soon as the main solution has passed through, pour this on the paper. When these washings have passed through, fill the filter once with cold water, and, as soon as this passes through, titrate the solution with potassium permanganate.

As the permanganate is added to the solution, it gradually changes color, and finally becomes colorless. A few additional drops of the permanganate will now impart a faint pink to the solution, indicating that the reaction is complete. From the amount of permanganate used, the percentage of phosphorus in the sample is obtained.

40. Titration With Nitric Acid.—Wash the yellow precipitate four times with a 2-per-cent. solution of nitric acid, and then four times with a 1-per-cent. solution of potassium nitrate. Remove the filter containing the yellow precipitate to a beaker, add standard sodium-hydrate solution in sufficient quantity to completely dissolve the precipitate, and stir with a glass rod until the filter paper is broken up into a pulp. About 30 cubic centimeters of the standard sodium hydrate will usually be sufficient. It should be added from a burette, and the amount used should be carefully noted. Dilute the solution to 75 or 100 cubic centimeters with water, add a few drops of phenol-phthalein, and titrate with a standard solution of nitric acid that exactly matches the standard sodium hydrate. The quantity of sodium hydrate used to dissolve the precipitate, minus the amount of nitric acid required to neutralize the excess of sodium hydrate, gives the amount of sodium hydrate actually needed to dissolve the precipitate, and, from this, the percentage of phosphorus is calculated.

41. Weighing the Yellow Precipitate.—As ammonium phospho-molybdate, precipitated as above directed, contains 1.63 per cent. of phosphorus, it may be weighed, and the phosphorus thus determined. If this method is employed, filter through a paper that has been dried at 110° in an air bath for 1 hour, and weighed quickly between matched glasses. Wash the precipitate from six to ten times with a 2-per-cent. solution of nitric acid, place the filter containing the precipitate on a piece of porcelain in an air bath, dry for 1 hour at 110° , and weigh quickly between matched glasses. The increase over the first weight is the weight of the yellow precipitate, and as this contains 1.63 per cent. of phosphorus, the percentage of phosphorus in the sample is readily calculated from this weight.

SOLUTIONS FOR PHOSPHORUS DETERMINATIONS

42. Acid Ammonium Sulphate.—To make up the acid ammonium-sulphate solution used in washing the yellow precipitate, add 27 cubic centimeters of concentrate ammonia

to $\frac{1}{2}$ liter of water; then slowly add 25 cubic centimeters of concentrate sulphuric acid, and dilute the solution to 1 liter with cold water. After mixing the solution well, and allowing it to cool, it is ready for use.

43. Standard Potassium Permanganate.—When the yellow precipitate is acted on by nascent hydrogen, generated by the zinc and sulphuric acid, the molybdic oxide is reduced to a lower oxide, the exact composition of which is still in doubt, but which appears to be $Mo_{12}O_{19}$. When permanganate is added to this, the molybdenum is oxidized to molybdic oxide again, probably according to the equation:

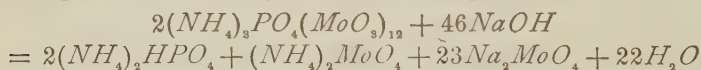


At all events, 34 molecules of $KMnO_4$ produce 60 molecules of MoO_3 . From this we see that 2 molecules of permanganate, which oxidize 560 parts of iron, will produce 508.23 parts of MoO_3 from the reduced oxide; or, the strength of a permanganate solution in terms of molybdic oxide is 90.76 per cent. of its strength in terms of iron. As the yellow precipitate contains 1.794 per cent. as much phosphorus as molybdic oxide, the strength of the permanganate solution in terms of phosphorus is 1.628 per cent. of its strength against iron. From this the percentage of phosphorus may readily be calculated when the titration is performed with any permanganate solution of known strength. In practical work, however, it is much more convenient to make a permanganate solution of such strength that 1 cubic centimeter = .006141 gram of iron. Its strength against molybdic oxide is 90.76 per cent. of this, or .005574 gram, and its strength against phosphorus is 1.794 per cent. of this, or .0001 gram.

To make such a solution, dissolve .8597 gram of ferrous ammonium sulphate, which contains .12282 gram of iron, in 150 cubic centimeters of water and 15 cubic centimeters of concentrate sulphuric acid, titrate with the permanganate, and dilute until just 20 cubic centimeters are required to oxidize the iron in this quantity of ferrous ammonium

sulphate. To make the permanganate solution, dissolve 3.5 grams of pure potassium permanganate in water, dilute to a little less than 1 liter, and let it stand in a cool dark place 2 or 3 days before the first titration. When this is diluted until 20 cubic centimeters of it just oxidize .12282 gram of iron, 1 cubic centimeter of it represents .0001 gram of phosphorus. After standardizing the solution in this way, it is best to test it against a standard steel or iron in which the phosphorus has been repeatedly determined gravimetrically, by weighing as magnesium pyrophosphate.

44. Sodium Hydrate and Nitric Acid.—Ammonium phospho-molybdate is a precipitate of varying composition; but when prepared as described, it has a composition represented by the formula $(NH_4)_3PO_4(MoO_3)_{12}$, which when dried at a low temperature retains 1 molecule of water and therefore contains 1.63 per cent. phosphorus. Sodium hydrate decomposes it according to the following reaction:



Since 46 molecules of sodium hydrate correspond to 2 molecules of ammonium phospho-molybdate, and therefore to 2 atoms of phosphorus, it follows that for every atom of phosphorus 23 molecules of sodium hydrate are required. It was seen in *Quantitative Analysis*, Part 2, that a normal solution of sodium hydrate contains in 1 liter the molecular weight, in grams, of $NaOH$. If, then, we have a sodium-hydrate solution 23 times as strong as a normal solution, it will contain sufficient sodium hydrate to correspond to 31 grams phosphorus per liter, or .031 gram of phosphorus per cubic centimeter. Such a solution is obviously far too strong. As a solution 1 cubic centimeter of which corresponds to .0002 gram phosphorus is desired, calculate the strength of the solution required in terms of a normal solution by the proportion $.031 : .0002 = 23 : x$. $x = .1483$. Therefore, a solution .1483, or 14.83 per cent., normal is the one required.

The solid sodium hydrate almost always contains some

carbonate. The solution required here should contain no carbonate, and it is best to prepare a strong stock solution as follows: Dissolve about 80 grams sodium hydrate in 500 cubic centimeters of water, add to this a saturated solution of barium hydrate as long as a precipitate forms. Transfer to a bottle having a rubber stopper, dilute to 1 liter, stopper tightly, shake the bottle, and allow the precipitate to settle. While this is settling prepare, according to the methods given in *Quantitative Analysis*, Part 2, a 14.83-per-cent. normal nitric acid.

When the barium carbonate has completely settled in the stock solution of sodium hydrate, draw off 200 cubic centimeters of the clear solution, dilute to 2 liters, mix thoroughly, and determine its strength against the 14.83-per-cent. normal nitric acid. Then continue the dilution until the sodium hydrate is the same strength as the nitric acid, and is therefore 14.83 per cent. normal. Each cubic centimeter of this solution corresponds to .0002 gram phosphorus.

While, as a rule, many chemists standardize the alkali solution against a weighed amount of pure ammonium phosphomolybdate, or against a standard sample of iron in which the phosphorus has been carefully determined and that is obtained through one of the standard laboratories, others, for reasons of their own, prefer the method given.

MANGANESE

45. The three methods most frequently used for the determination of manganese in iron are Ford's method, Volhard's method, and the color method. Ford's method is regarded as the most reliable, and is very largely used in settling disputes, establishing standards, etc., but it is too long to be very largely used in doing the routine work of an iron-works laboratory. Volhard's method, if properly carried out, yields very accurate results, and is sufficiently short to be largely employed in routine work. The color method is not generally considered as reliable as the other methods in the case of iron, but, on account of the rapidity with which

it yields results, it is quite largely used as a guide in manufacturing processes, and, in the hands of an experienced chemist, it yields very satisfactory results.

46. Ford's Method.—Dissolve 5 grams of the drillings in 65 cubic centimeters of nitric acid of 1.2 Sp. Gr., and boil until the solution becomes almost syrupy; then add 100 cubic centimeters of nitric acid of 1.42 Sp. Gr., boil for a few moments, and add from 5 to 10 grams of potassium chlorate to the boiling solution, a little at a time, to precipitate the manganese as dioxide. When precipitation is complete, the greenish-yellow gas above the liquid gives a puff and disappears. Now add 1 gram more of potassium chlorate, boil 1 or 2 minutes, and cool rapidly by standing the beaker in cold water. When the solution has become cold and the precipitate has settled, filter through asbestos, and from this point proceed as directed in Art. 25.

47. Volhard's Method.—Dissolve 1.5 grams of the drillings in a porcelain dish in 25 cubic centimeters of nitric acid of 1.2 Sp. Gr., and when the violent action ceases, add 12 cubic centimeters of half-strength sulphuric acid; evaporate to dryness, and ignite until dense white fumes of SO_2 are given off. Allow the residue to cool, add 100 cubic centimeters of water, and boil until solution is complete. When cool, wash the solution into a 300-cubic-centimeter graduated flask, nearly neutralize the acid with a concentrate solution of sodium carbonate, and add an emulsion of zinc oxide in water until the mixture assumes the color of coffee with cream. Dilute with water to exactly 300 cubic centimeters, mix thoroughly, and pour the solution through a large fluted filter placed in a dry funnel, receiving the filtrate in a clean dry beaker. By means of a pipette, transfer 200 cubic centimeters of this solution to a 500-cubic-centimeter flask, heat to boiling, and titrate with potassium permanganate, shaking it well after each addition of permanganate, to cause the precipitate formed to collect and settle rapidly. A pink tinge in the clear liquid above the precipitate indicates the

end of the reaction. The titration must be rapid, so that the solution has no chance to cool.

48. The Color Method.—Weigh out .2 gram of standard iron in which the manganese has been carefully determined, and pour it into a 10-inch test tube; then place exactly the same weight of the sample to be tested in a similar test tube, and dissolve each in 25 cubic centimeters of nitric acid of 1.2 Sp. Gr. When violent action ceases, stand the tubes on a sand bath heated by a good burner, or suspend them over Argand burners, and, after solution is complete, boil them gently until the yellowish fumes are entirely expelled from the tubes. Then add about 2 grams of lead peroxide to each and continue the boiling for 3 minutes. The lead peroxide oxidizes the manganese to permanganic acid, which has the well known color of potassium permanganate. Cool the solutions rapidly by standing the test tubes in cold water.

When the solutions are cool, and the insoluble matter has completely settled, decant the standard into a graduated reading tube having an inside diameter of about $\frac{1}{2}$ inch, and dilute it until each cubic centimeter of the solution represents .01 per cent. of manganese. For example, if the standard iron contains .3 per cent. of manganese, dilute the solution to 30 cubic centimeters. Then decant the solution to be tested into a similar reading tube, and dilute it until it has exactly the same color as the standard. Each cubic centimeter of this solution will then represent .01 per cent. of manganese; thus, if the solution is diluted to 35 cubic centimeters to make the colors agree, the sample contains .35 per cent. of manganese. If care is taken in decanting the solutions from the test tubes to the reading tubes, all but 2 or 3 drops of the liquid may be decanted without introducing any of the insoluble matter.

Instead of heating the samples over a burner or on a sand bath, the tubes are sometimes stood in a solution of calcium chloride that boils at 115° . In this way, the solutions may be boiled without danger of breaking the tubes. It is scarcely

necessary to add, that, in order to obtain correct results, the standard and the sample to be tested must be treated in as near the same manner as possible.

CARBON

49. Carbon is not usually determined in pig iron, but occasionally the percentage of this element is required. When this is the case, it is determined by one of the combustion methods given under Steel, using 1 gram of the sample and a corresponding amount of solvent. The color method for carbon is not applicable in the case of pig iron.

STEEL

50. Although steel is usually more regular than pig iron in composition, it is still far from homogeneous in many instances, and, consequently, in taking a sample, drillings from different parts of the piece sampled should be obtained if possible. The bottom of an ingot seldom has exactly the same composition as the top, and the center of a rod or wire usually differs in composition from the metal at the surface. These irregularities in composition should always be taken into account when selecting a sample for analysis. A sample of steel is not so likely to contain sand as is pig iron, but it may contain scale, and, if this is present, the sample should be freed from it by means of the magnet, as in the case of pig iron.

The principal determinations made in the analysis of steel are *silicon*, *sulphur*, *phosphorus*, *manganese*, and *carbon*. Silicon is less frequently determined than the other elements, but its estimation is important in some cases. Sulphur and manganese are determined in steel in exactly the same way that they are estimated in iron, and, as the determination of these elements in pig iron has been thoroughly described, they will not be treated at this point. It should be stated, however, that the color method for manganese is considered more reliable in the case of steel than when

applied to pig iron. In fact, for the routine work in steel-works laboratories, it is used much more than any other method.

It is frequently stated that the color method is only accurate for samples containing less than 1 per cent. of manganese, but chemists that have used this method largely, usually regard it as reliable in the case of all samples containing less than 2 per cent., and some experiments seem to show that it will yield satisfactory results with samples containing even higher percentages. A standard steel, having, approximately, the same percentage of manganese as the sample tested, should always be used; hence, it is best to have several standards containing different quantities of manganese. Sometimes samples of iron are compared with a steel standard, but, as a rule, it is best to compare samples of steel with a steel standard, and samples of iron with an iron standard. Aside from what has just been said, in determining sulphur and manganese in steel, the directions given for the determination of these elements in iron should be followed exactly.

SILICON

51. Weigh 5 grams of the drillings into a porcelain dish, cover it with a watch glass, add 50 cubic centimeters of nitric acid of 1.2 Sp. Gr., and 35 cubic centimeters of half-strength sulphuric acid, and evaporate rapidly over an Argand burner until the solution begins to bump; then turn out the flame, remove the cover, and stir the syrupy solution vigorously for a few moments, when it will solidify. Or, after adding the acid, stand the dish on a sand bath, with the cover drawn to one side, and allow it to slowly evaporate to dryness. In either case, heat the residue over an Argand burner until dense white fumes are given off. When cool, add 30 cubic centimeters of half-strength hydrochloric acid and about 75 cubic centimeters of water; heat until solution is complete, and boil the solution a few minutes to make sure that all iron salts are dissolved. Filter through a small ashless filter, wash first with half-strength hydrochloric

acid, then once with water, then again with half-strength hydrochloric acid, and, finally, wash five or six times with water. Wrap the filter around the precipitate, place them in a platinum crucible, and, after burning off the paper, ignite intensely over a blast lamp. Cool in a desiccator and weigh as silica SiO_2 , which contains 47.02 per cent. of silicon.

Sometimes a correction is made as follows: Dissolve the precipitate of SiO_2 in hydrofluoric acid, add 2 or 3 drops of sulphuric acid, evaporate to dryness, ignite, cool, and weigh again. If the determination is properly performed, this is unnecessary, for, in this case, the result obtained by the correction will seldom, if ever, differ from the first result; and, if there is a difference, it will be very slight.

PHOSPHORUS

52. The phosphorus in steel may be determined by any of the methods described for the determination of this element in iron, and one of these methods is generally employed. In addition to these, however, Dr. Drown has proposed a method in which the phosphorus is oxidized and the organic matter destroyed by potassium permanganate in a nitric-acid solution, and, on account of its rapidity, this method is quite largely employed. Other methods of oxidizing the phosphorus in solution have also been proposed, but none of these have come to be used so generally as that proposed by Dr. Drown. It has been stated that some samples of steel—notably, those containing a high percentage of carbon—do not yield all their phosphorus when oxidized by any of these wet methods, but this objection does not appear to be proven. Dr. Drown's method yields very accurate results with ordinary steel, and many chemists consider it perfectly reliable in all cases. Others, however, prefer to use one of the methods given for the determination of phosphorus in iron, until the objection mentioned has been more thoroughly investigated. These methods are applied to steel in exactly the same way that they are to iron.

53. Drown's Method.—Weigh 2 grams of the drillings into a 12 or 16 ounce Erlenmeyer flask, add 75 cubic centimeters of nitric acid of 1.13 Sp. Gr., and, after violent action ceases, boil the solution for 2 or 3 minutes. Add 10 cubic centimeters of a potassium-permanganate solution containing about 12 grams to the liter, and continue the boiling until the pink color of the permanganate is destroyed. If the solution becomes clear, more permanganate must be added, and the boiling continued until a brown precipitate forms, when oxidation of phosphorus and carbon will be complete. Remove the flask from the heat for a moment, and add pure ferrous sulphate, in very small portions, until the precipitate is nearly dissolved; then boil it again for a few moments until the solution becomes perfectly clear. Remove the flask from the heat, and, after a minute or two, cautiously add 10 cubic centimeters of ammonia of .90 Sp. Gr., allowing the ammonia to run down the side of the flask, to avoid loss by spattering.

Boil the solution again for a few moments, to completely dissolve the iron precipitate; then insert a thermometer and allow the solution to cool to 85°. When at exactly this temperature, add 50 cubic centimeters of ammonium-molybdate solution, causing it to rinse off the thermometer as it flows into the flask. Give the flask a rotary motion for a few moments, then close it with a clean rubber stopper, and shake vigorously for 5 minutes. Allow the precipitate to settle for 15 minutes, filter, and wash thoroughly with the acid ammonium-sulphate solution described in Art. 42. Wash as much of the precipitate as is convenient into the flask in which the precipitation was made, and dissolve the portion adhering to the paper with dilute ammonia, adding enough ammonia to dissolve all the precipitate; then wash the filter thoroughly with water, allow the ammonia and washings to run into the flask with the main part of the precipitate, and stir this until the precipitate is completely dissolved.

To this solution add about 12 grams of granulated zinc and 80 cubic centimeters of dilute sulphuric acid (1 part of

concentrate acid to 3 parts of water), place a small funnel in the neck of the flask, and stand it in a warm place for half an hour. Reduction will now be complete. Pour the solution through a large fluted filter, to separate the undissolved zinc. Rinse the flask with pure cold water, pour this on the filter, and, when it has run through, wash the filter by filling it once or twice with pure cold water. The filtrate, which should amount to from 300 to 400 cubic centimeters, is titrated at once with permanganate. As the permanganate is added, the solution gradually changes color and finally becomes colorless, when a few more drops of permanganate will impart a pink tinge to it, showing that the reaction is complete.

The solutions used in this determination are the same as those employed for the determination of phosphorus in iron, and the calculations are the same, except, in this case, 2 grams of the sample are taken.

This method is frequently modified by passing the solution of the yellow precipitate through a reductor instead of reducing it by heating in a flask with zinc and sulphuric acid.

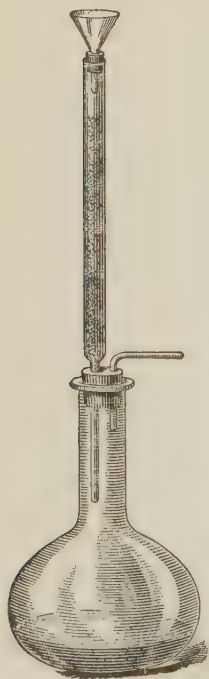


FIG. 9

54. The Reductor.—At the present time, chemists are beginning to use a reductor quite largely to reduce solutions. A simple form of reductor is shown in Fig. 9. It is made as follows: Draw out a piece of glass tubing having an inside diameter of about $\frac{1}{2}$ inch; cut it off at a point about 15 inches from the end, and pass the small portion of the tube thus drawn out through one of the perforations of a rubber stopper fitted in a filtering flask. Drop in a few pieces of broken glass that are too large to pass through the small part of the tube, and, on this,

pour about 1 inch of coarse quartz sand that has been thoroughly cleansed (first, by boiling in hydrochloric acid, and then washing with distilled water) and thoroughly dried. On this, pour about 12 inches of pure granulated zinc that will pass through a 20-mesh but not through a 30-mesh sieve, and close the tube with a singly perforated stopper through which the stem of a funnel is passed. When a solution containing acid is poured in the funnel and drawn through the column of zinc, it is completely reduced at once, and, after washing the zinc thoroughly, is ready for titration.

To use the reductor in the determination of phosphorus by the method just given, dissolve the yellow precipitate in ammonia as directed, add about 50 cubic centimeters of dilute sulphuric acid (1 part acid to 3 parts water), dilute to 200 cubic centimeters, pour it in the funnel and draw it through the reductor by means of the filter pump. Wash all the solution out of the reductor by drawing 200 cubic centimeters of water through it, and titrate the solution at once with permanganate. The reagents used destroy some permanganate, and the amount thus used up must be determined by means of blanks, and deducted from the amount of permanganate used in the titrations. Several blanks, containing, approximately, the same amount of each of the reagents, and about the same amount of free acid, and having, approximately, the same bulk as the solution to be titrated, should be passed through the reductor and titrated. The first blank will generally use more permanganate than the succeeding ones; if this is the case, this result should be discarded, and the average of the others taken as the amount of permanganate to be deducted in each case.

CARBON

55. Unlike any of the other elements contained in steel, carbon is known to exist in at least two conditions in the metal, in forms known as *graphite* and *combined carbon*. It is also believed that the combined carbon exists in two modifications, which are known as *hardening* and *cement*

carbon, and recent investigations have made this view appear almost certain.

It was noticed that when steel was worked, the results obtained in determining the combined carbon by the color method differed during the working, and that the properties of the steel also differed. It appears that the carbon shown by the color method is the part of this element present that imparts to the steel the property of becoming hard when tempered, and has received the name of *hardening carbon*. The color method is used almost exclusively for the determination of carbon in the routine work of steel-works laboratories, and, as the amount of graphite in steel is very small, and cement carbon, if such a form exists, is not known to have any influence on the properties of the metal, the results obtained by this method are usually reported merely as *carbon*.

From what has been said, it is evident that analytical chemistry supplies the means of distinguishing between at least two forms of this element in steel; viz., combined carbon and graphite, and it now seems probable that the color method only gives a part of the combined carbon, known as *hardening carbon*. For a long time the results obtained by the color method were supposed to represent all the combined carbon, and at present the percentage thus obtained is usually spoken of as the *combined carbon*. Accurate combustion methods are used for the determination of the total carbon, and the graphite; and from these results, the combined carbon is obtained by difference.

Three combustion methods are given. The first one—burning the carbonaceous residue in oxygen—is the most generally used, but the apparatus is costly, and the results obtained by the other methods, the apparatus for which is less expensive, are almost, if not quite, as accurate.

The carbon is not very often determined in pig iron, but if desired, either of the combustion methods here given may be used equally well for this purpose. In determining the carbon in pig iron, spiegeleisen, etc., 1 gram of sample and a corresponding amount of solvent should be used.

Otherwise, the determinations should be carried out exactly as here given.

56. Total Carbon.—Weigh out 3 grams of the fine drillings, add 200 cubic centimeters of an acid solution of the double chloride of copper and potassium, and stir until the copper thrown out at first is all redissolved. The solution may be accomplished in a beaker, a 16-ounce Erlenmeyer flask, or a heavy glass jar. The drillings should be very fine for this determination, for fine drillings yield more uniform results, and, with coarse drillings, the process of solution becomes very tedious. If necessary, a few more drops of acid may be added, and the mixture heated to 80°. When the copper is all taken up by the solution, allow it to stand a few minutes to settle, and then proceed by one of the following methods:

1. *Combustion in Oxygen.*—Filter on a felt of pure ignited asbestos in a platinum boat shown in Fig. 10, leaving as much of the carbon as possible in the vessel. Add 10 cubic

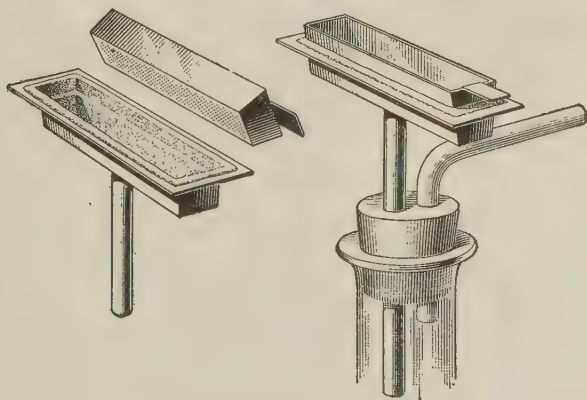


FIG. 10

centimeters of hydrochloric acid of 1.1 Sp. Gr. to the vessel in which the sample was dissolved, and so manipulate that this acid shall touch every part of the vessel that has come in contact with the solvent liquid. Pour this acid on the felt in the boat, wash the carbon upon the felt by means of

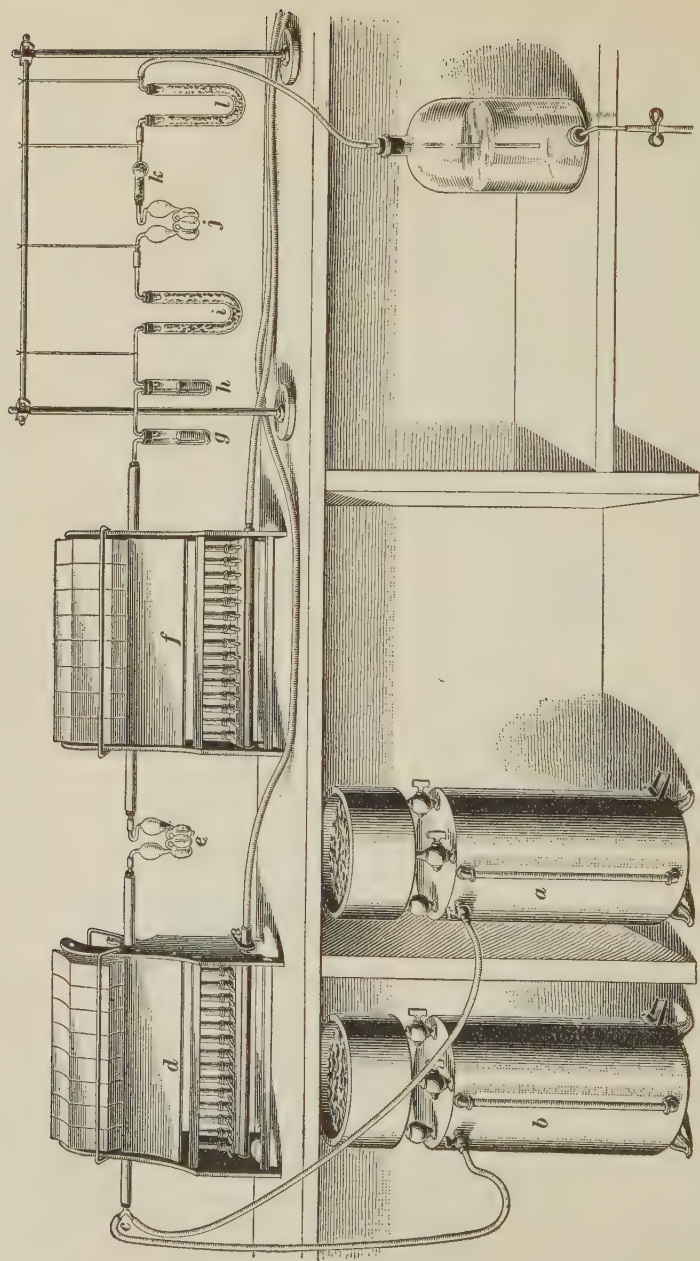


FIG. 11

a wash bottle containing the same strength acid, and continue to wash with this acid until the washings come through perfectly clear. Then wash with water until the washings no longer react for hydrochloric acid when tested with silver nitrate. Dry the carbon, and filter by placing the boat in an air bath heated to about, but not above, 100° . While this is drying, weigh the absorption bulb and prolong, and place them in their proper position in the carbon train, which is shown in Fig. 11, and is prepared as follows:

The gasometers *a* and *b* contain air and oxygen, respectively, and are connected with the Y tube *c*, which passes through a rubber stopper in the end of the porcelain tube fitted in the combustion furnace *d*, known as the preheating furnace. This tube should project at least 5 inches at each end of the furnace to prevent the rubber stoppers from becoming hot, and contains 8 or 10 inches of granulated copper oxide. Next comes the Geissler bulb *e* containing a strong solution of potassium hydrate, and known as the *purifying bulb*.

This is connected with the combustion tube proper, placed in the combustion furnace *f*. It is a tube of royal Berlin porcelain of $\frac{5}{8}$ inch internal diameter, and glazed inside and out. If a 14-inch Bunsen furnace is used, the tube should be from 24 to 28 inches long, and should be so placed that at least 5 inches of it project at each end of the furnace. To prepare this tube, place three or four tightly fitting disks of copper gauze towards one end of it, pour about 4 inches of granulated copper oxide on to them, and hold this in place by placing three or four more disks of copper gauze against it. Next to these, place a roll of pure silver gauze (about 2 inches in length) that nearly fills the tube, and place the tube in the furnace so that the gases evolved when the carbon is burned will pass through the roll of silver and the copper oxide. To the combustion tube attach a bubble tube *g* filled to about one-half its capacity with an acid solution of ferrous sulphate, to catch any free chlorine that may escape from the combustion tube, and connect this with a second bubble tube *h* filled to nearly one-half its capacity

with silver sulphate and water, to absorb any hydrochloric acid that may be mixed with the carbon dioxide. Tightly stoppered test tubes may be made to serve for the bubble tubes.

Next attach a **U** tube *i* filled with dry granulated calcium chloride, to dry the gas. To this, attach the weighed Geissler absorption bulb *j* containing a solution of potassium hydrate, and connect this with the weighed prolong *k*, which is filled with pure granulated calcium chloride that has been dried for half an hour in a platinum or porcelain dish over a Bunsen burner. Care must be taken not to fuse the calcium chloride while drying it. Different parts of the same lot of calcium chloride should be used to fill the prolong and the tube *i*, so that their drying power will be the same, and, whenever one of these tubes is refilled, the other should also be refilled from the same lot of calcium chloride. To the prolong, attach a **U** tube *l*, also filled with calcium chloride, to prevent any moisture from entering the combustion train from this end, and attach this **U** tube to an aspirator. All connections must be perfectly tight, so that gas can neither enter, nor escape from, the apparatus, and the ends of the glass tubes should come as near as possible to meeting inside of the rubber tubing used for connections. The pressure in the gasometers *a* and *b* should be so regulated that it will force air or oxygen through the purifying bulb *e*, but will not force them through the bubble tubes *g* and *h*.

When ready to commence a combustion, light the burners of the preheating furnace *d*, and gradually increase the temperature until the combustion tube containing copper oxide is red hot for 5 or 6 inches of its length. Then place the platinum boat containing the carbon next to the roll of silver foil in the combustion tube of the furnace *f*, and close the connection. Start the combustion by lighting enough burners, under the part of the tube in the furnace *f* that contains the copper oxide, to embrace about 3 inches of it in flame. Then see that the connection between the air gasometer and the preheating furnace is closed; turn on the oxygen, and regulate the aspirator so that about three bubbles per second

pass through the bulb *j*. The heat and aspiration must be so regulated that a steady current of oxygen passes through the bulb *e*, and there must not be back pressure at this point at any time during the operation. When the tube over the burners has become fairly red, turn on two more burners, and, when the tube has become red above these, turn on the burners one at a time, allowing the tube to become red above each burner before the next one is turned on, until the tube under the boat, and for 2 or 3 inches back of it, is embraced in flame.

After the tube has become red over all the burners lighted, allow the combustion to proceed for from 20 to 40 minutes, depending on the amount of carbon to be burned. Now, turn off every second burner, stop the supply of oxygen, turn on the air, and aspirate until about 1.5 liters of air have passed through the absorption bulb *j* at the rate of about three bubbles per second. While the aspiration is going on, turn out additional burners as fast as possible, without danger of breaking the tube from too sudden cooling. When the required amount of air has passed through, remove the absorption bulb and prolong, cover each end with a short piece of rubber tubing, one end of which is closed, with a piece of glass rod, stand them in the balance case 15 minutes to assume the temperature of the balance, and weigh. The increase in weight is the weight of carbon dioxide CO_2 , produced by the combustion of the carbon, and contains 27.27 per cent. of carbon. When 3 grams of sample are taken, the weight of carbon dioxide, divided by 11, and the result multiplied by 100, gives the percentage of carbon in the sample.

Before making a determination by this method, two blanks should be run, and if the weight of the bulb and prolong changes to any great extent, something is wrong with the apparatus or chemicals. When two blanks are run without changing the weight of the absorption bulb and prolong more than 1 milligram, the last weight obtained in running the blank may be taken as the first weight in making a determination.

Dr. C. B. Dudley, to whom we are indebted for this

method, advises the use of a small absorption bulb and prolong, the whole, when filled and ready for use, to weigh from 50 to 60 grams.

2. *Combustion by Chromic Acid.*—Pour the solution in which the carbon is suspended through a felt of pure ignited asbestos in a filtering tube, prepared as shown in Fig. 5, leaving as much as possible of the carbon in the vessel in which solution was accomplished. To the carbon in this vessel, add 10 cubic centimeters of hydrochloric acid of 1.1 Sp. Gr. and so manipulate that the acid shall touch every part of the vessel that has come in contact with the solvent liquid. Pour this through the filter, wash the carbon on to the asbestos by means of a wash bottle containing acid of the same strength, and continue to wash with this acid until the washings are colorless as they come through. Then wash with distilled water for some time after the washings cease to give a reaction for hydrochloric acid when tested with silver nitrate. Transfer the carbon and asbestos to the flask *a*, using not more than 20 cubic centimeters of water to rinse in the carbon, and place the flask in position in the carbon train, shown in Fig. 12.

The flask *a* containing the carbon is fitted with a doubly perforated stopper, through one perforation of which the funnel tube *b* is passed. This is connected with the U tube *c*, which is filled with lumps of fused potassium hydrate, and acts as a purifying tube. Through the other perforation in the stopper of the flask *a*, is passed a tube connecting with the bubble tube *d*, containing pyrogalllic-acid solution to absorb free chlorine and chlorine compounds of chromium. The bubble tube *e* is filled to a little less than half its capacity with an acid solution of ferrous sulphate, and *f* is a similar bubble tube, filled to a little less than half its capacity with an acid mixture of silver sulphate and water. The U tube *g* is filled with pure, dry, granulated calcium chloride.

Next comes the Geissler absorption bulb *h*, containing a strong solution of potassium hydrate, and to this is attached the prolong *i*, containing pure, dry, granulated calcium chloride. The absorption bulb and prolong are weighed

before they are introduced into the train. The prolong is connected with the U tube *j*, containing granulated calcium chloride, to prevent the entrance of moisture at the end of the train, and this is connected with an aspirator. A weighing U tube, filled to two-thirds its capacity with soda

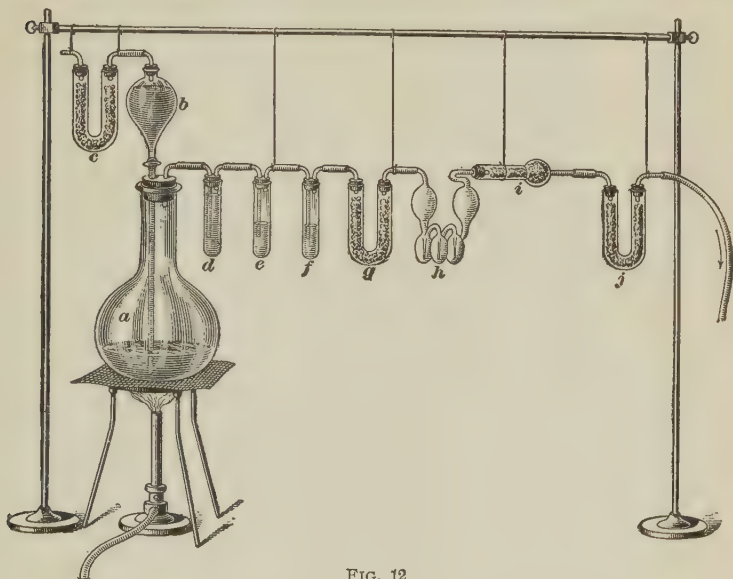


FIG. 12

lime and the other one-third with granulated calcium chloride, is sometimes substituted for the absorption bulb and prolong, but this change is not to be recommended. In making connections, bring the ends of the glass tubes as near together as possible, under the rubber tubing, and be sure all connections are perfectly tight before commencing a determination.

When all is in readiness, remove the stopper from the separatory funnel *b*, introduce 10 cubic centimeters of a saturated solution of chromic anhydride CrO_3 , allow it to flow into the flask *a* containing the carbon, and close the stop-cock. Now pour 100 cubic centimeters of concentrate sulphuric acid that has been heated nearly to boiling with a little chromic anhydride, into the separatory funnel, insert

the stopper carrying the purifying tube *c*, and, by turning the stop-cock, allow the acid to pass slowly into the flask *a*. Use the aspirator if necessary. Do not, under any circumstances, allow any gas to pass out through the separatory funnel. Keep air passing through the apparatus so that about three or four bubbles per second show in the absorption bulb. After a few moments, bring a burner, turned very low, under the flask *a*, and gradually increase the temperature until the acid mixture just begins to boil, and maintain this temperature for 10 or 15 minutes.

The carbon will now all be converted into carbon dioxide CO_2 by the oxidizing mixture. Gradually lower the flame of the burner, and, finally, turn it out, keeping the current of air through the apparatus constant, however. When about 1 liter of air has passed through the absorption bulb after the light is extinguished, disconnect the absorption bulb and prolong; cover each end with a short piece of rubber tubing, the other end of which is closed with a piece of glass rod, stand them in the balance case 15 minutes to assume the temperature of the balance, and weigh. The increase in weight is the weight of carbon dioxide CO_2 from the combustion of the carbon, and contains 27.27 per cent. of carbon. When 3 grams of sample are taken, the percentage of carbon may be calculated by dividing the weight of carbon dioxide by 11, and multiplying the result by 100.

This method is not generally considered as reliable as the first one, but the apparatus is simpler and less expensive, and when carefully performed by a skilled analyst, it yields very accurate results.

3. *Combustion in Platinum Crucible.*—This method was originated by Dr. W. P. Shimer, and the description of the method and apparatus employed is mainly taken from the Journal of the American Chemical Society, and the catalogue of the Baker and Adamson Chemical Company, who control the patents on the Shimer apparatus.

At first the special water-cooled stopper was used with an ordinary platinum crucible, the upper part being cooled by a wet wick wrapped around it. The special water-jacketed

crucible, while increasing the cost of the apparatus, is a decided improvement.

The Shimer combustion apparatus comprises a special platinum crucible, provided with a copper, brass, or silver stopper and rubber-band seal. The upper edge of the platinum crucible is bent outwards and back upon itself, forming a cooling chamber about $\frac{1}{8}$ inch wide and $\frac{1}{2}$ inch deep. Short platinum inlet and outlet tubes are attached to opposite points of this chamber for the ingress and egress of a cooling stream of water. The copper stopper is hollow and provided with inlet and outlet tubes for the circulation of cooling water within its walls, and for the entrance and exit of gases to and from the interior of the crucible. The side wall of the stopper is tapered, and slightly smaller in diameter at its base than the opening in the crucible, the space between the two being filled and made gas-tight by means of a rubber gasket or band stretched around the base of the stopper. The circulation of

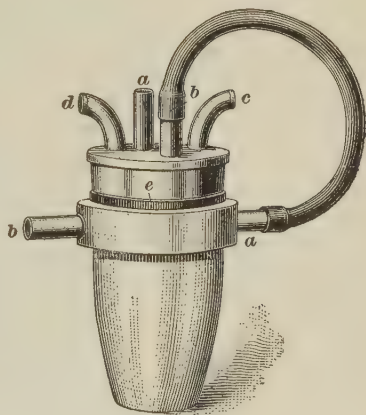


FIG. 13

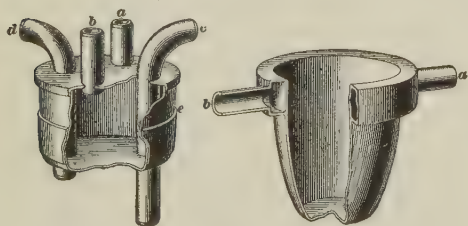


FIG. 14

the blast lamp without in the least affecting the rubber band, or the security of the seal. The construction and arrangement of the several parts of the apparatus are clearly shown in Figs. 13 and 14. *a* and *b* are the inlet and outlet tubes

cooling water within the stopper and the water-jacket surrounding the upper edge of the crucible permits the lower part of the crucible to be heated to the full temperature of



FIG. 15

for the circulation of cooling water; *c* and *d* are, respectively, the inlet and outlet tubes for the transmission of the air and the products of oxidation; *e* is the rubber gasket or band of pure black rubber, such as can be obtained from stationers.

Fig. 15 shows the complete apparatus for the combustion. It consists of the following parts, beginning at the left:

1. Two aspirator bottles, the upper filled with distilled water and the tube leading to the lower bottle extending to the bottom of the latter.

2. Potassium-hydroxide bulbs containing potassium hydroxide of 1.27 specific gravity.

3. A little guard bottle to retain any drops of potassium hydroxide that may be forced over from the Geissler bulbs.

4. The combustion crucible connected with its reservoir of water for supplying the stopper; the piece of stout asbestos board perforated to support the crucible at a point about half-way through. Under the crucible is placed the blast lamp.

5. Next to the crucible is the cupric-oxide tube, a short brass tube, 10 to 12 inches long, of small diameter, filled in its middle portion with cupric oxide. The ends of this tube are kept cool by pieces of wick wrapped around them; the wick is kept wet by having the ends dip in beakers of water. The brass tube is filed down at the ends and the rubber tubing is stretched over them. The tube is supported across the top of a tripod, with a single good Bunsen burner with flared top below, to heat to a red heat $1\frac{1}{2}$ to 2 inches of the cupric oxide. A piece of stout asbestos board is laid across the top of the tripod to retain the heat.

6. Next to the cupric-oxide tube is a glass tube filled with glass beads, wet with water, and kept quite cold externally by wet wick, to retain chlorine and hydrochloric acid. The wick is wrapped about the tube, the free ends hanging in a beaker of distilled water.

7. A large calcium-chloride tube.

8. The potassium-hydroxide bulbs or soda-lime tube.

9. A guard tube of calcium chloride.

From 2 to 3 grams of drillings are treated with double chloride of copper and potassium as previously directed.

The carbon is filtered upon asbestos in the following manner: A glass rod about 1 inch longer than the stem of the funnel (an ordinary funnel, $2\frac{1}{2}$ inches in diameter) and small enough in diameter to pass easily through the stem, is flattened out at one end and notched at two or three places by pressing the red-hot glass against the sharp corner of a file.

In preparing the filter, very short-fibered ignited asbestos is used, with fibers not longer than $\frac{1}{16}$ inch. This is well stirred with distilled water so as to have it well in suspension in a rather large bulk of water. A small piece of dry asbestos about the size of a pea is placed in the bottom of the funnel upon the end of the glass rod; this is to prevent the finely divided and suspended asbestos from packing into the passage, thus impeding filtration. The suction is now turned on and a little of the suspended asbestos is poured on. When this has been deposited as a fine horizontal felt, pour on more asbestos. If the asbestos fibers are short enough, a perfectly tight filter may be made with not more than $\frac{1}{4}$ inch of asbestos. A small bulk of filter greatly facilitates subsequent transference and combustion. When dry, the carbon may usually be picked off in a thin shell by means of a pair of forceps; it is easily transferred to the empty crucible with the carbon side down. It is well to have a circular piece of thin platinum foil in the bottom of the crucible. The small amount of carbon remaining in the funnel is removed by use of a little ignited asbestos. It is necessary to be careful to keep all the carbon within about $\frac{1}{4}$ inch from the bottom of the crucible, which is not at all difficult to do. If a part of the carbon were to be $\frac{1}{2}$ to $\frac{3}{4}$ inch from the bottom, it might escape complete combustion. Graphitic carbon from pig iron is easily burned in air at the white heat attainable by the blast lamp. After the carbon is all transferred, a little ignited asbestos is filled in on top of it.

Another way is to add a little finely divided, ignited asbestos to the solution, and to filter the carbon on a Gooch crucible. The Gooch, without its cap, is then placed on the

bottom of the combustion crucible. This method has the advantage of rapid filtration, quick transference, and avoidance of contact of the carbon and traces of copper oxide with the bottom of the combustion crucible. A Gooch crucible may be made out of an old ignition crucible.

While the funnel containing the carbon, after being washed, is drying, connect up the apparatus and test it as follows: Fill the crucible one-third full of ignited asbestos and close it, first wetting the rubber band. A little wet wick wrapped several times about each end of the brass cupric-oxide tube inside of the rubber connections and hanging in beakers of water, will avoid all risk of burning. The moisture tube is disconnected and filled with cold distilled water, and the excess is allowed to drain out by holding the tube in a vertical position. Open the clamp and allow water to run through the stopper. Now put the Bunsen flames under the crucible and the middle of the cupric-oxide tube, covering the latter with a piece of asbestos board. Open the clamp between the upper and lower aspirator bottles and leave it fully open. Open the clamp between the lower aspirator bottle and the potassium-hydroxide bulb and regulate the passage of air by this clamp alone. Let air bubble through the apparatus, at the rate of 3 bubbles per second, for 20 minutes. Detach and weigh absorption apparatus with the usual precautions. A second weight nearly always agrees well with the first. When the constant weight is obtained, the carbon is transferred to the crucible as described and the combustion is begun, after, of course, testing the apparatus for tightness. Before putting the stopper into the crucible it is best to wet the rubber band with the wet finger. This prevents friction and insures a tight crucible. Be sure that water is running from the stopper and that the cupric-oxide tube is red hot for from $1\frac{1}{2}$ to 2 inches, then turn on the air at the speed of about 3 bubbles per second and bring a small blast-lamp flame immediately under the crucible so as to heat the bottom to a bright-red heat, extending at least $\frac{1}{4}$ inch from the bottom. A large flame is to be avoided. The bottom of

the crucible should be flat or, better, slightly convex—never concave. Combustion begins immediately, and in 1 or 2 minutes carbon dioxide begins to be absorbed by the potassium-hydroxide bulbs. Combustion is complete in 25 minutes or less. At the end of this time remove the blast lamp and aspirate 4 liters of air through the apparatus. Then detach and weigh the absorption apparatus with the usual precautions. The increase in weight is the CO_2 , which contains 27.27 per cent. carbon. In removing the asbestos from the

crucible there is often, when copper solution has been used for dissolving the sample, a black residue remaining where the carbon was, which may mislead the inexperienced, but it is oxide of copper, as is easily proved by its solubility in strong hydrochloric acid.

When the carbon, after filtration, is well washed both with hydrochloric acid and hot water, there is very little chlorine or hydrochloric acid to fear, and the moisture tube effectually stops it. After every five or six combustions, it is only necessary to rinse out the tube with distilled water and connect it again. The tube is 6 inches long and $\frac{3}{4}$ inch in diameter.

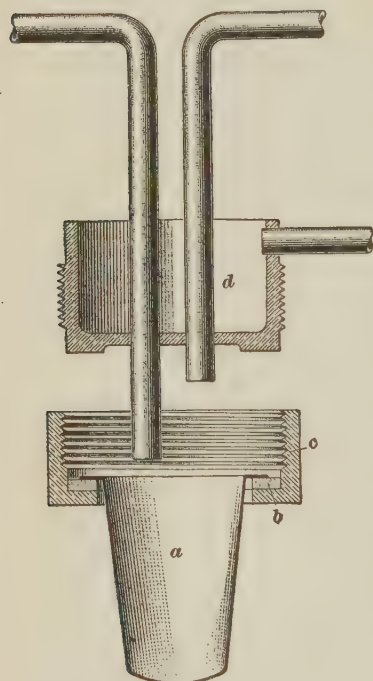


FIG. 16

The two bulbs are empty; the tube itself is filled with glass beads of about $\frac{1}{8}$ inch in diameter; it retains about $2\frac{1}{2}$ cubic centimeters of water when drained.

This method of combustion in a platinum crucible has been largely introduced in iron and steel-works laboratories, and yields excellent results. Great care, however, must be

taken not to heat the upper part of the crucible enough to burn the rubber band. To avoid this danger and at the same time furnish a less costly piece of apparatus, John V. R. Stehman has devised the ignition crucible and water-cooled stopper shown in Fig. 16.

The crucible *a* is of platinum with a flange around the top. At *b* is shown a washer made of a piece of acid-washed, asbestos wick yarn. This is moistened, laid on the flange of casing *c*, and then pressed into place by screwing *d* down upon it, the crucible being left out. This flattens the washer and forces out the excess of moisture. The crucible is now dropped into place and *d* moved down upon it. The bottom of *d* is turned true and polished and makes an air-tight joint with the crucible and asbestos washer. Water is supplied to the cooling cup by a tube reaching to the bottom of the cup and connected with the water reservoir. This tube is not shown in the figure. This crucible may be substituted for Shimer's model and the determination carried out as just described.

57. Graphite.—There are two methods for the determination of graphite in steel and pig iron that are more or less used, and both are here given. The first method, according to which the sample is dissolved in hydrochloric acid, is the most largely used, but the second method, in which the sample is dissolved by nitric acid, yields the most uniform, and probably the most accurate, results. The details of the two methods are as follows:

1. *Solution in Hydrochloric Acid.*—Dissolve 1 gram of pig iron, or from 5 to 10 grams of steel, in hydrochloric acid of 1.1 Sp. Gr., using 25 cubic centimeters of the pig iron, or 15 cubic centimeters for each gram of steel taken. Cover the beaker, and boil for 10 or 15 minutes. Filter on an asbestos felt in a platinum boat or filtering tube, washing the carbon on to the asbestos with a jet of hot water. Wash alternately on the felt with hot water and hydrochloric acid of 1.1 Sp. Gr., and then wash two or three times with hot water to remove the hydrochloric acid. Now wash the

precipitate with a solution of potassium hydrate of 1.1 Sp. Gr. until all effervescence, due to silicon, ceases; wash the potassium hydrate out of felt with hot water, then wash twice with alcohol and twice with ether, and, finally, wash with hot water until the last trace of ether is removed from the precipitate and filter. If a direct combustion method is to be used, dry it at a temperature slightly below 100° , introduce it in a combustion tube or crucible, and burn it in oxygen or air, following the directions previously given. If combustion by chromic acid is used, transfer the asbestos and carbon to a flask, using not more than 20 cubic centimeters of water to wash it in, and oxidize the carbon by means of chromic anhydride and sulphuric acid, following the directions given in Art. 56, 2. In either case, the increase in weight of the absorption bulb and prolong is the weight of carbon dioxide obtained. From this, calculate the percentage of carbon, and call the result *graphite*.

2. *Solution in Nitric Acid*.—Weigh 1 gram of pig iron, or from 5 to 10 grams of steel, into a beaker, and dissolve in nitric acid of 1.2 Sp. Gr., using 25 cubic centimeters for the pig iron, or 15 cubic centimeters for each gram of steel taken. Stand aside until the residue settles, filter on a felt of ignited asbestos in a platinum boat or a filtering tube, washing the carbon on to the asbestos with hot water, and wash thoroughly on the filter with hot water. Then wash the residue with a solution of potassium hydrate of 1.1 Sp. Gr., follow this treatment by washing several times, alternately, with hot water and hydrochloric acid of 1.1 Sp. Gr., finally washing the acid out of the filter with hot water. Next wash twice with alcohol, then twice with ether, and, finally, wash thoroughly with hot water. If direct combustion is to be used, dry it at a temperature slightly below 100° , place it in a combustion tube or crucible, and burn in oxygen or air as previously directed. If combustion by chromic acid is used, transfer the asbestos to a flask, using less than 20 cubic centimeters of water to rinse the carbon in, and oxidize by means of chromic anhydride and sulphuric acid, following the directions given in Art. 56, 2. In either case, calculate

the percentage of carbon found from the weight of carbon dioxide, shown by the increase in weight of the absorption bulb and prolong, and call the result *graphite*.

58. Combined Carbon.—Having determined the total carbon and the graphite in a sample, the combined carbon is obtained indirectly by subtracting the graphite from the total carbon. This process would be much too long for general use in a steel-works laboratory, and, for the routine work, the color method is universally employed. This method, as we have already pointed out, probably only gives a part of the combined carbon, but, as this is not certain, and as the part shown by this method is supposed to be the only part exerting any important influence on the character of the steel, the results obtained by it are at present reported as combined carbon.

59. The Color Method for Carbon.—The color method depends on the fact that when a sample of steel is dissolved in pure nitric acid of 1.2 Sp. Gr., it imparts to the solution a depth of color that is directly proportionate to the amount of combined carbon it contains. Hence, the amount of combined carbon may be determined by comparing the color of the solution of the sample to be analyzed with the color of the solution of a sample in which the carbon has been carefully determined by combustion methods. There are several things, however, that have an influence on the color produced. The method of solution, the chemical composition of the steel, the physical treatment it has received, and the process by which it was manufactured, all appear to have their influence on the color produced; hence, the standard steel should have, approximately, the same composition, should have been manufactured by the same process, and receive the same physical treatment, and should be dissolved in the same manner and at the same time as the samples to be tested. The best results are obtained when both the standard steel and the samples for analysis are taken as the metal is poured into the mold.

A number of modifications of this method have been published, and are used, and many of them have advantages for steels of certain composition. One that the writer has used very largely, and found to give excellent results with samples of any composition, is as follows:

Weigh out .5 gram of the standard steel, and exactly the same weight of each of the samples for analysis; transfer each to a properly labeled test tube $\frac{7}{8}$ inches long by $\frac{7}{8}$ inch in diameter, and stand the test tubes in a rack similar to the one shown in Fig. 17, in which *a* is a copper disk perforated to receive the test tubes, and *b*, which is joined to the copper disk by the supports, is a disk of coarse copper gauze for the test tubes to rest on.

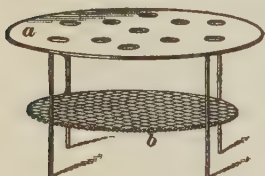


FIG. 17

Place the rack containing the test tubes with the samples in a vessel of cold water, and add 10 cubic centimeters of nitric acid of 1.2 Sp. Gr. to each. The nitric acid used for this purpose should be perfectly pure, and under no conditions must it contain chlorine or hydrochloric acid. When violent action ceases, place the rack containing the tubes in a water bath containing boiling water, and leave them in this for 5 minutes after all the steel is dissolved, shaking the tubes occasionally, if necessary, to prevent the formation of a film of iron oxide. Stand the rack in a dish of cold water 2 minutes for the solutions to cool, decant the standard into a graduated reading tube of colorless glass, and dilute it until 1 cubic centimeter of the solution represents .01 per cent. of carbon.

Thus, if the standard contains .15 per cent. of carbon, dilute the solution to 15 cubic centimeters with distilled water. Now decant one of the samples to be tested into a similar reading tube that has exactly the same dimensions as the one containing the standard, and dilute it until its color exactly matches the standard. Each cubic centimeter of this will now represent .01 per cent. of carbon. Thus, if the solution amounts to 18 cubic centimeters, the sample

contains .18 per cent. of combined carbon. As soon as the reading is taken, this tube should be emptied, rinsed, a second sample introduced, diluted, and read in the same way.

Not more than 10 samples should be analyzed at once, and the readings should be taken as rapidly as possible, for the standard gradually loses its color when allowed to stand. The colors should be compared in diffused light. It is best to stand in front of a window facing north, when comparing them, and a piece of wet filter paper pressed against the back of the tubes sometimes helps to determine the exact tint. A camera, shown in Fig. 18, is sometimes used for this purpose. It consists of a box of light wood, blackened inside. About 1 inch from the end *b*, a piece of ground glass is inserted. Just back of this, two openings are made in the top to receive the comparison tubes. By viewing the solutions from the end *a*, the tints are determined.

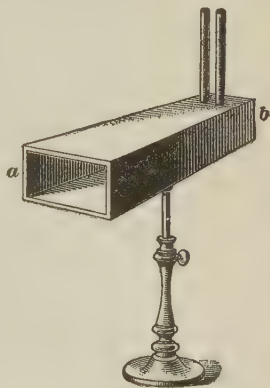


FIG. 18

If the steel contains more than .4 per cent. of combined carbon, it is best to use samples weighing .2 or .3 gram, and dissolve them in 5 or 6 cubic centimeters of nitric acid. As it takes some time, as a rule, to dissolve samples containing so much carbon, it is best to place small glass bulbs in the mouth of the tubes to prevent loss of acid by evaporation during solution. In reading such samples, dilute the standard until 1 cubic centimeter represents .02 or .03 per cent. of carbon, dilute the sample until the colors agree, and multiply the reading by the factor. For instance, let us suppose that the standard steel contains .6 per cent. of carbon, and the solution is diluted to 20 cubic centimeters. Each cubic centimeter will then represent .03 per cent. of carbon. If the solution of a sample, when diluted to match this, amounts to 22 cubic centimeters, it contains $22 \times .03 = .66$ per cent. of combined carbon.

SOLUTIONS FOR CARBON DETERMINATIONS

60. Copper Potassium Chloride.—To make the acid copper-potassium-chloride solution, used in dissolving the sample for the determination of total carbon, dissolve 1 pound of solid salt in 1,300 cubic centimeters of water, and, if the solution is not perfectly clear, filter through ignited asbestos. To the clear solution or filtrate, add 100 cubic centimeters of pure concentrate hydrochloric acid, and stir well to secure thorough mixing.

61. Potassium Hydrate.—The potassium-hydrate solution used in the absorption bulb, and in the purifying bulb, is made by dissolving pure solid potassium hydrate in a small amount of water, and diluting the solution until it has a specific gravity of 1.27 when cold. About 1 liter of this solution may be made from 400 grams of solid potassium hydrate.

62. Ferrous Sulphate.—To make the acid solution of ferrous sulphate, dissolve the pure crystallized salt in water, making almost a saturated solution, and to every 50 cubic centimeters of this solution add 5 drops of concentrate sulphuric acid. This solution is used to absorb free chlorine. It appears to form hydrochloric acid, and to retain most of the acid thus formed.

63. Silver Sulphate.—Doctor Dudley recommends the following method for the preparation of this solution: Precipitate silver carbonate by adding sodium carbonate to a solution of silver nitrate. Filter and wash thoroughly. By means of a little water, transfer the precipitate to the bottle in which it is to be kept, and add sulphuric acid—at last, drop by drop—while agitating the mixture, until the carbonate is completely decomposed and the liquid is distinctly acid to test paper. To fill the bubble tube, shake the bottle well and pour enough of the milky mixture into the tube so that about $\frac{1}{4}$ inch of solid will settle to the bottom; then add water to fill the tube to nearly one-half its capacity. This

solution absorbs any hydrochloric acid that may pass over from the ferrous-sulphate tube.

64. Pyrogallie-Acid Solution.—This solution is made up by mixing .2 gram of pyrogallie acid, 5 grams of neutral potassium oxalate, and 3 grams of pure sodium chloride, and dissolving the mixture in water sufficient to make 20 cubic centimeters of solution. When dissolved, add 2 drops of concentrate sulphuric acid, which must render the solution distinctly acid to test paper. This solution absorbs free chlorine and chlorochromic acid. It may liberate hydrochloric acid, as it tends to form this acid from the oxides of chlorine.

ANALYSIS OF COAL AND COKE

PROXIMATE ANALYSIS

65. A proximate analysis of coal is nearly always required, and, although the results obtained are, to a great extent, merely comparative, yet, when the directions given are strictly followed, the results obtained are accurate enough to be of great service in determining the value of the coal for various purposes. It is of the utmost importance that the directions given should be followed exactly in every case, for slight variations in the method give large differences in the results, and as the results, so far as *moisture*, *volatile combustible matter*, and *fixed carbon* are concerned, are only comparative, they must be obtained under exactly the same conditions in every case if they are to be of any value.

In selecting a sample, about 5 pounds of the coal should be taken, exercising care, of course, to get a sample representing the whole quantity. Break this up and quarter it down until a sample weighing about 100 grams is left. Pulverize this, and keep it in a tightly stoppered bottle until analyzed. The quartering and pulverizing should be carried out as rapidly as possible, to prevent the absorption or loss

of water, and, as coal in the powdered form changes in other respects, especially when exposed to air, it should be kept in a tightly stoppered bottle, and the analysis should be made as soon as convenient after the sample is taken. A method of analysis that gives concordant results, and is probably more largely used than any other at the present time, is as follows:

66. Moisture.—When coal is dried at a temperature slightly above 100° , it loses in weight for a time, and then begins to grow heavier. Consequently, we cannot dry the sample in the ordinary way until a constant weight is obtained, and it is necessary to dry all samples for a certain time at a fixed temperature to obtain concordant results. The following method of doing this has been generally adopted: Weigh 1 gram of the pulverized sample into a porcelain or platinum crucible. Place the crucible, uncovered, in an air bath having a temperature ranging from 104° to 107° , and heat it at this temperature for exactly 1 hour. Place the crucible in a desiccator, cover it, and allow it to cool. As soon as cool, weigh covered, and call the loss in weight *moisture*.

67. Volatile Combustible Matter.—Weigh 1 gram of the pulverized sample into a clean platinum crucible, weighing 20 to 30 grams and having a tightly fitting cover. Place the cover on tight, and heat over a good Bunsen burner for exactly 7 minutes. The burner should be adjusted so that it gives a good flame 20 centimeters high. The crucible should be supported, but on a platinum triangle, so that the bottom is 7 centimeters above the top of the burner. The determination should be made in a place that is as nearly free from drafts as possible. Cool the crucible in a desiccator and weigh as soon as cool. From the loss in weight caused by this treatment, subtract the amount of moisture found, and call the remainder *volatile combustible matter*. This determination should always be made on a fresh sample of coal, and not on the sample used for the determination of moisture.

68. Fixed Carbon and Ash.—After weighing the crucible for the determination of volatile combustible matter, draw the cover a little to one side, place the crucible in an inclined position on a triangle, so as to admit a plentiful supply of air, place a good Bunsen burner under it, and heat until the carbon is completely burned off. This operation is likely to prove tedious, and may be hastened by letting the crucible cool from time to time, and by stirring the contents with a stout piece of platinum wire, taking care, of course, not to lose any of the material in the crucible while stirring it up. Care must also be taken not to produce too strong a current of air in the crucible while heating it, as, in this way, particles may be carried out, and a fictitious value given to the coal or coke by the apparent increase in fixed carbon and decrease in ash. When the residue in the crucible no longer shows any unburned carbon, heat it a few minutes longer, then cool it in a desiccator and weigh. The difference between this weight and the last one is the weight of fixed carbon in the sample, and the substance remaining in the crucible is ash. The percentages of the different constituents are, of course, calculated in the usual manner, and, as 1-gram samples are taken, the calculations are very simple. The sum of the percentages of fixed carbon and ash is approximately the percentage of coke that may be obtained from the coal.

69. Sulphur.—There are two methods in quite general use for the determination of sulphur in coal and coke. They are known as the fusion method and Eschka's method. The fusion method is the older, and, until quite recently, was used almost exclusively, but at the present time Eschka's method is much the more generally used. Both methods are given herewith.

1. *The Fusion Method.*—Weigh out 1 gram of the pulverized sample, mix it thoroughly with 9 grams of sodium carbonate and 5 grams of potassium nitrate, by grinding them together in a mortar, and transfer the mixture to a large platinum crucible. Rinse out the mortar by grinding

in it about 1 gram of sodium carbonate, and pour this on the mixture in the crucible. Cover the crucible and heat it over a Bunsen burner. A very gentle heat should be applied at first, and the temperature should be raised gradually, removing the cover from time to time to see that the fusion does not boil over. None of the fusion must be allowed to get on the outside of the crucible, or it will absorb sulphur from the burning gas and cause the analysis to yield erroneous results. For the same reason, care should be taken not to allow the gaseous products of the combustion to enter the crucible. When the contents of the crucible are in a state of quiet fusion, run the mass well up on the sides of the crucible, and allow it to cool.

Dissolve the fusion out of the crucible with hot water, wash the crucible thoroughly, boil the fusion until it is completely disintegrated, filter off the insoluble matter, and wash it thoroughly on the filter with hot water. Acidulate the filtrate with hydrochloric acid, and evaporate to dryness. Moisten the residue with a few drops of hydrochloric acid, add about 100 cubic centimeters of water, and heat to boiling. Filter, wash the filter well with hot water, dilute the filtrate to about 400 cubic centimeters, heat it to boiling, and precipitate the sulphur by adding from 10 to 20 cubic centimeters of a 10-per-cent. solution of barium chloride. Stand the solution in a warm place for the precipitated barium sulphate to settle, filter through a paper, or an asbestos felt in a Gooch crucible, ignite moderately, observing the precautions necessary in the ignition of this precipitate, cool, and weigh as barium sulphate $BaSO_4$, which contains 13.73 per cent. of sulphur.

A blank determination should be made with each new lot of chemicals, using the same amount of each that is used in the actual determination; and the weight of barium sulphate that is obtained from the blank determination is subtracted from the weight obtained in each sulphur determination of the coal, before the percentage of sulphur in the coal or coke is calculated.

2. *Eschka's Method*.—Weigh out 1 gram of the pulverized coal or coke and mix thoroughly with 1.5 grams

of Eschka mixture (see Art. 71) in a thin platinum dish of from 75 to 100 cubic centimeters capacity. A large crucible may be used instead of a dish. Support the dish on a triangle and heat slowly, holding the burner in the hand at first. If the gas ordinarily used contains sulphur—and all coal gas does contain this element—an alcohol lamp should be used, and not a Bunsen burner. Stir the mixture frequently with a platinum wire and keep the flame in motion, only touching the dish with the flame until strong glowing has ceased. Then gradually increase the heat until, in about 15 minutes, the bottom of the dish is at a low red heat. Keep at this temperature, stirring every few minutes with the platinum wire, until the carbon has completely burned; this will usually require about 1 hour. When the carbon is completely burned, allow the dish to cool, transfer the mass to a beaker, and rinse out the dish, using about 50 cubic centimeters of water. Add 15 cubic centimeters of a saturated solution of bromine in water, boil for 5 minutes, allow to settle, decant the clear liquid through a filter, add 30 cubic centimeters of water to the residue in the beaker, boil 5 minutes, allow to settle, decant the clear liquid through the filter, and boil the residue again for 5 minutes with 30 cubic centimeters of water. Filter through the same paper and wash until a few drops of the liquid running through the funnel gives no precipitate when acidified with nitric acid and tested with silver nitrate. The total volume of the liquid in the beaker under the filter should now be about 200 cubic centimeters. Add 2 cubic centimeters of concentrate hydrochloric acid and boil until the bromine is completely expelled. Test a drop of the liquid with litmus paper to make sure that it has an acid reaction. If not acid, add 1 or 2 drops hydrochloric acid and again boil. When all the bromine has been driven off and the liquid is slightly acid, add slowly to the solution, which should be kept at about the boiling point, 10 cubic centimeters of a 10-per-cent. solution of barium chloride. Stir constantly while adding the barium chloride, and add it slowly, not more than 1 drop a second.

Stand the beaker in a warm place for the precipitate to

settle; filter, wash thoroughly with hot water acidulated with a few drops of hydrochloric acid, ignite moderately, and weigh as barium sulphate $BaSO_4$, which contains 13.73 per cent. of sulphur. The directions previously given should be followed in filtering and igniting this precipitate.

Although chemicals that are absolutely free from sulphur may be obtained for this determination in the market, a careful blank should be run with each new lot of reagents, for some so-called C. P. ("chemically pure") chemicals are not strictly as represented.

70. Phosphorus.—Weigh out 10 grams of the powdered sample in a platinum crucible, and burn off the carbon. This may be done as in the determination of fixed carbon, or, if the laboratory contains a muffle furnace, the crucible may be placed in this and the carbon allowed to burn, leaving the crucible uncovered in this case. As samples of anthracite coal and coke burn very slowly, the process is sometimes hastened by burning in oxygen. This may be done by covering the crucible with a perforated piece of platinum foil, and leading a slow current of oxygen through this perforation, in the same way that the hydrogen is led into the Rose crucible in the ignition of copper sulphide (see this determination).

When all the carbon is burned off, treat the residue with concentrate hydrochloric acid, dilute the solution with water, filter, wash thoroughly with hot water, and stand the filtrate aside. Dry the filter and residue, burn off the paper, and fuse the residue with about six times its weight of pure sodium carbonate. Dissolve the fusion in water, filter off the insoluble matter, and wash it well with hot water. Acidulate the filtrate with hydrochloric acid, and evaporate to dryness. Moisten the residue with a few drops of hydrochloric acid, add about 100 cubic centimeters of water, boil a few minutes, and filter. Wash the insoluble matter on the filter with hot water, and add this filtrate to the first one. To the combined filtrates, add a little ferric chloride that must be free from phosphorus, and render the solution

slightly alkaline with ammonia; then acidulate it with acetic acid, and boil a few minutes.

The precipitate formed will contain all the phosphorus. Filter and wash once with boiling water. Dissolve the precipitate in hydrochloric acid, and evaporate the solution to a small bulk, taking care not to allow an insoluble scale of iron oxide to form. Then add 5 cubic centimeters of concentrate nitric acid, and follow this in a few moments with 30 cubic centimeters of water. Filter into a flask and wash the filter well with a 2-per-cent. solution of nitric acid. To the solution in the flask, add 30 cubic centimeters of concentrate ammonia, and then about 1 cubic centimeter of concentrate nitric acid in excess of the amount required to dissolve the precipitate formed. Heat the solution to exactly 85°, add from 50 to 75 cubic centimeters of ammonium-molybdate solution, agitate the solution for 5 minutes, allow it to stand 15 or 20 minutes for the precipitate to settle, filter, wash, and proceed with the determination by one of the methods given in Art. 36, *et seq.* It is best to use the gravimetric method, weighing as magnesium pyrophosphate, for this determination, and the directions given in Art. 16 should be followed. When using this method, if the percentage of phosphorus is low, it is best to allow the solution to stand about 1 hour for the yellow precipitate to settle.

REAGENTS FOR COAL ANALYSIS

71. Eschka Mixture.—Weigh out a convenient quantity of pure magnesium oxide that must be free from sulphur, and that has been previously ignited to expel all moisture; add to this half its weight of pure dry sodium carbonate, grind them together until they are thoroughly mixed, and keep the mixture in a tightly stoppered bottle. A bottle with a ground-glass stopper is preferred for this purpose; at all events, the mixture must be kept dry.

72. Calorific Value of Coal.—The determination of the heating power of coal involves the use of expensive

apparatus and delicate manipulation. Such determinations will not be treated in this Course; but we give a method of calculating the heating power of coal from its proximate analysis that, on most samples, gives results very close to the results of actual measurements made with utmost care. Several formulas for making this calculation from the results of analysis have been suggested. On the whole the most satisfactory is that of Goutal, modified by De Paepe.

Let M = percentage of volatile matter;

N = percentage of volatile matter calculated on the coal supposed to be deprived of water and ash.

P = calorific power of coal;

C = percentage of fixed carbon;

A = a coefficient which varies according to the value of N .

$$N = \frac{100M}{M + C}$$

$$P = \frac{8,150C + AN}{100}$$

$$A = 14,000 \text{ for } N = 2 \text{ to } 12$$

$$A = 12,000 \text{ for } N = 12 \text{ to } 17$$

$$A = 11,000 \text{ for } N = 17 \text{ to } 24$$

$$A = 10,200 \text{ for } N = 24 \text{ to } 30$$

$$A = 9,400 \text{ for } N = 30 \text{ to } 35$$

$$A = 8,000 \text{ for } N = 35 \text{ to } 38$$

$$A = 7,900 \text{ for } N = 38 \text{ to } 40$$

$$A = 7,600 \text{ for } N = 40 \text{ to } 50$$

The result here, P , gives the calories set free by the combustion of 1 kilogram of coal. This multiplied by 1.8 gives the B. T. U. liberated by the combustion of 1 pound.

LIMESTONE

73. The analysis of limestone has been described in *Quantitative Analysis*, Part 4. The determinations usually required are silica, alumina, iron, lime, and magnesia.

BLAST-FURNACE CINDER

74. Most samples of blast-furnace cinder are easily decomposed by hydrochloric acid. With samples that are exceptions to this rule the cinder must be fused with sodium carbonate before treating with hydrochloric acid.

1. *Silica*.—Weigh .5 gram of the finely powdered cinder, transfer it to a porcelain casserole, or dish, add 20 cubic centimeters of water, and stir until every particle of the sample is thoroughly wet. Add slowly, and with constant stirring, 30 cubic centimeters of hydrochloric acid (1 : 1). In most cases the sample will dissolve to a clear solution, often in a few minutes setting to a clear jelly-like mass. Add 1 cubic centimeter of nitric acid, cover with a watch glass, and heat over an Argand burner until all the water has been driven off. Allow to cool, add 3 cubic centimeters of hydrochloric acid, and again evaporate to dryness. This evaporating to dryness twice is absolutely necessary in order to thoroughly decompose the silicic acid. Cool, add 20 cubic centimeters of concentrate hydrochloric acid and 40 cubic centimeters of water. Heat to nearly the boiling point for 3 minutes, filter, wash free of chlorine, transfer the wet paper and precipitate to a platinum crucible, heat first at a low temperature and finally intensely until all the paper is burned. Cool and weigh. The weight of the precipitate multiplied by 200 gives the percentage of silica SiO_2 , provided exactly .5 gram of the sample was taken.

2. *Alumina*.—The filtrate from the silica, which should be about 200 cubic centimeters in a 400-cubic-centimeter beaker, is covered with a watch glass and heated to boiling. Add a slight excess of ammonia, and continue the boiling for 2 minutes. Remove from the heat and allow to settle. Decant the clear liquid through a filter, wash the precipitate, first by decantation, and finally on the paper with hot water until free from chlorine. Transfer the precipitate and paper to a platinum crucible, heat first at a low temperature and finally intensely until the paper is burned. Cool and weigh as Al_2O_3 . This precipitate will contain any iron

that might be in the cinder; but the amount of this is so small that it is generally disregarded.

3. *Lime*.—Heat the filtrate from the alumina to boiling, add 25 cubic centimeters of a saturated solution of ammonium oxalate and 10 cubic centimeters concentrate ammonia. Complete the determination of calcium oxide as described in the analysis of limestone.

4. *Magnesia*.—Treat the filtrate from the calcium oxalate for magnesia as described in the analysis of limestone.

In reporting results of a cinder analysis the percentages of insoluble silicious matter—alumina Al_2O_3 , lime CaO , and magnesia MgO —are generally given.

DETERMINATIONS OCCASIONALLY REQUIRED IN ORES AND PIG IRON

75. Alumina in Iron Ores.—This determination is sometimes required and is best accomplished in the following manner: Unite the filtrates from the silica determination and evaporate or dilute to 400 cubic centimeters. To the cold solution, add ammonia until it becomes dark red, but contains no precipitate. Add 3.3 cubic centimeters of hydrochloric acid, 1.2 specific gravity, and 2 grams of sodium phosphate, which should be dissolved in water and filtered. Now add 10 grams of sodium thiosulphate dissolved in water and filtered, if necessary, and 15 cubic centimeters of acetic acid, 1.04 specific gravity, heat to boiling, boil 15 minutes, filter as rapidly as possible, wash thoroughly with hot water, dry, ignite in a porcelain crucible, and weigh as $AlPO_4$, which contains 41.85 per cent. of Al_2O_3 .

76. A Rapid Method for the Approximate Determination of Graphite.—Frequently in foundries determinations of graphitic carbon are required, and while the methods referred to give the best results, quicker methods, in which the graphite is weighed directly, generally give results exact enough for practical purposes. Probably the most satisfactory method of this kind is due to Crobaugh,

and is carried out as follows: 2 grams of the iron is dissolved in a 400-cubic-centimeter beaker with 100 cubic centimeters of nitric acid of 1.135 specific gravity, heating if necessary, but keeping the volume of the liquid constant by the addition of water if there is any evaporation. When the solution is nearly complete, add 3 cubic centimeters of strong, chemically pure, hydrofluoric acid, taking care not to pour it against the glass. Give the beaker a whirling motion, and the solution will generally be complete in a few minutes. Filter, using the pump, through counterpoised filter, placing both papers in the funnel, one under the other. Transfer the graphite completely to the paper, wash four times with water, then twice with hot hydrochloric acid of 1.10 specific gravity, then with water, then twice with ammonia (1 volume of concentrate ammonia to 2 volumes of water), then twice with hydrochloric acid, and finally wash clean with water. Allow the last of the wash water to run through, remove the papers from the funnel, spread them out on a glass plate, and shift the under paper so that the lines of folding do not coincide with those of the upper paper. Dry in an air bath at exactly 100° C. Place the under paper on the balance pan on which the weights are placed and the paper with the graphite on the other pan. The difference in weight is the graphite. In case all silica is not removed by the hydrofluoric acid, the paper with the graphite may be burned and the silica left weighed and subtracted.

To get counterpoised filter: Take two best quantitative filter papers of the same size, place one in each balance pan; find out which is the heavier, and with a clean sharp pair of scissors trim the heavier paper until it just balances the other.

QUANTITATIVE ANALYSIS

(PART 6)

Serial 201F

Edition 2

ANALYSIS OF CLAY

CHEMICAL ANALYSIS

1. Clay is principally a product of the decomposition of feldspathic rocks, and is essentially a mixture of the silicates of aluminum, calcium, magnesium, sodium, and potassium with silica. The silicates are hydrated, so that clay ordinarily contains from 6 to 14 per cent. of combined water, and nearly all, if not all, samples contain small quantities of iron. A mechanical analysis of clay to separate the coarse from the fine parts, and a careful examination to determine the condition in which the silica exists, as well as a number of tests of physical properties, are sometimes required; but for these the student is referred to a more exhaustive treatise on the subject, and only the chemical analysis will be given here. This is ordinarily all that is required to determine the fitness of the clay for the manufacture of bricks, or for use in metallurgical operations. Clay that is to be used for the manufacture of firebrick, or in metallurgical processes where it is exposed to great heat, should not contain much iron, potassium, or sodium, as these constituents fuse rather easily. The best clay for these purposes does not contain more than 1 per cent. of either of the alkalis, or more than 2 per cent. of iron oxide. The determinations usually made are, moisture, combined water,

silica, alumina, iron oxide, calcium oxide, magnesia, and the alkalies.

2. Determination of Moisture.—Grind from 5 to 10 grams of the clay to an exceedingly fine powder in an agate mortar, weigh it on a watch glass, transfer the watch glass with the sample to an air bath, and heat it for one hour at a temperature ranging from 100° to 105° . Remove it to a desiccator, and weigh as soon as cool. Return the watch glass with the sample to the air bath, heat it 15 minutes longer at the same temperature, cool in a desiccator, and weigh again as soon as cool. If this weight differs from the previous one, the sample must be heated again, and this must be continued until a constant weight is obtained. From the loss in weight when the sample is dried at this temperature, calculate the percentage of moisture in the sample.

As soon as the sample is weighed, transfer it to a clean dry bottle or tube, and keep it tightly stoppered, to be used for the other determinations. As the other constituents are determined in the dry sample, the moisture is not included in the regular report, but is reported as a separate item.

3. Determination of Combined Water.—Weigh 2 grams of the dried sample in a platinum crucible, and ignite it for 20 minutes with the cover on, keeping the crucible at a red heat. Cool in a desiccator and weigh as soon as cool. Ignite 5 minutes longer, cool in a desiccator, and again weigh as soon as cool. If this weight differs from the previous one, the ignition must be continued until a constant weight is obtained. From the loss in weight, calculate the percentage of combined water in the sample. This method yields accurate results with most samples, but if the clay contains much organic matter or pyrite, it cannot be used. In such cases, the water should be determined by the method described under Prehnite in a former Section.

4. Determination of Silica.—Weigh out 1 gram of the dry sample, mix it thoroughly with 10 grams of fusion mixture, consisting of equal parts of the carbonates of sodium and potassium, and introduce the mixture into a large platinum crucible. Heat this over a good Bunsen burner until it begins to cake together, and then heat over a blast lamp until it has been in a state of quiet fusion for some time. The fusion may now be removed from the crucible by quickly pouring the molten mass into a clean dry platinum dish floating on cold water. The fusion, upon striking the cold platinum, solidifies quickly and will not adhere to the dish. The small quantity of fusion remaining in the crucible can be mostly removed by hot water, and the small quantity remaining after this treatment is readily dissolved out by hydrochloric acid.

At all events, dissolve the fusion in water, acidify the solution with hydrochloric acid, evaporate to dryness, and heat at about 130° until the odor of hydrochloric acid is no longer given off. To the residue, add 15 cubic centimeters of concentrate hydrochloric acid, and heat gently to dissolve the iron; then add 50 cubic centimeters of water, heat to boiling, allow the insoluble matter to settle, and filter. Wash thoroughly on the filter with hot water, wrap the paper around the precipitate, place them in a platinum crucible, and, after burning off the paper over a Bunsen burner, ignite intensely over a blast lamp, cool in a desiccator, and weigh as silica. From this weight, calculate the percentage of silica in the sample.

5. Determination of Alumina.—Heat the filtrate from the silica to boiling, add a few drops of concentrate nitric acid, then add a slight excess of ammonia while stirring continuously, and continue to boil for a few moments, taking care that the solution remains faintly alkaline. As soon as the precipitate has settled, decant as much as possible of the clear liquid through a filter, then transfer the precipitate to the filter, and wash it thoroughly with hot water. Wrap the filter around the precipitate, place them in a

platinum crucible, and, after burning off the paper over a Bunsen burner, ignite strongly over a blast lamp, cool in a desiccator, and weigh. The precipitate now consists of the oxides of aluminum and iron, $Al_2O_3 + Fe_2O_3$. After determining the ferric oxide in the sample, deduct this from the mixed oxides, and the remainder will be alumina.

The iron may be determined by fusing the precipitate of mixed oxides with acid potassium sulphate, dissolving the fusion, reducing the iron, and titrating with permanganate, as directed in a former Section under Feldspar, or the iron may be determined in a separate portion of the sample, as directed in Art. 8.

6. Determination of Calcium.—If the filtrate from the alumina greatly exceeds 250 cubic centimeters in volume, evaporate it to about this amount; then, to the gently boiling solution, add 5 cubic centimeters of concentrate ammonia, and a moderate excess of ammonium oxalate, continue the boiling for a few minutes, and then stand the solution in a warm place for 4 hours, to allow the precipitate to collect and settle. Slightly more ammonium oxalate than is required to convert all the calcium and magnesium into oxalates must be added, but a very large excess is to be avoided. Filter off the precipitated calcium oxalate, and wash it thoroughly with hot water to which a few drops of ammonia have been added. Wrap the precipitate in the filter, place them in a platinum crucible, and, after heating gently over the Bunsen burner, to drive off moisture and burn the paper, ignite at the full power of the blast lamp until a constant weight is obtained. It is a good plan to allow the precipitate to cool, after igniting it for 5 or 10 minutes over the blast lamp, and, when cool, to moisten it with a few drops of water; then, after heating it gently to drive off the water, ignite it again at the full power of the blast lamp for 10 minutes before weighing it the first time. When a constant weight is obtained, the precipitate is calcium oxide, and from this weight, the percentage of calcium oxide in the sample is obtained.

7. Determination of Magnesium.—Evaporate the filtrate from the calcium oxalate to about 200 or 250 cubic centimeters, cool the solution by standing the beaker in cold water, and, when cold, add an excess of sodium-ammonium phosphate, drop by drop, while stirring continuously. When all the reagent has been added, pour in a quantity of concentrate ammonia equal to about one-third the volume of the solution. Stir the solution several times after the ammonia is added, and then stand it in a cool place for 6 hours, for the precipitate to separate. Filter and wash the precipitate thoroughly with cold one-third-strength ammonia containing a little ammonium nitrate. Dry the precipitate in an air bath, remove it as completely as possible from the filter, and burn the latter in a weighed crucible. When this is cool, add the precipitate, ignite at the full power of the blast lamp for 10 minutes, cool in a desiccator, and weigh as magnesium pyrophosphate $Mg_2P_2O_7$. From this, calculate the percentage of magnesium oxide MgO in the sample.

8. Determination of Iron.—The iron may be determined in the precipitate of alumina and iron after it has been weighed, by fusing it, and proceeding as directed in Art. 5, or it may be determined in a fresh sample as follows: Fuse 1 gram of the sample with mixed carbonates, dissolve the fusion in water and hydrochloric acid, and evaporate to dryness, just as in the determination of silica. Moisten the residue with hydrochloric acid, dissolve it in water, filter off the silica, and wash it well with hot water, adding a few drops of hydrochloric acid with the fourth or fifth quantity of wash water. Heat the filtrate to boiling, add a few drops of concentrate nitric acid, and, after boiling the solution a few moments longer, precipitate the iron and alumina with ammonia.

As soon as the precipitate settles, filter and wash once or twice with hot water. Dissolve the precipitate in the least necessary quantity of hydrochloric acid, reduce the iron in this solution with zinc, and titrate with potassium permanganate in the usual way. A blank must be run to determine

the amount of permanganate used up by the reagents. The difference is the amount used by the iron. From the amount of iron found in this way, calculate the percentage of ferric oxide in the sample. The ferric oxide found by this determination is deducted from the alumina and iron oxide previously determined, to obtain the percentage of alumina.

9. Determination of Alkalies.—Weigh out 1 gram of the sample, place it in an agate mortar, add 1 gram of pure ammonium chloride, and grind them together intimately; then add 7 grams of pure calcium carbonate, and grind the contents of the mortar together with the pestle until thoroughly mixed. Now introduce 1 gram of pure calcium carbonate in the bottom of a large platinum crucible, pour the mixture from the mortar on this, and cover the mixture with 1 gram more of the pure calcium carbonate. Cover the crucible, place it over a Bunsen burner, turned very low at first, but gradually increase the temperature, and, finally, heat to dull redness for an hour. Treat the contents of the crucible with hot water in a porcelain dish, breaking up any hard lumps with an agate pestle, if necessary. After boiling until the mass is completely disintegrated, filter off the insoluble matter, and wash it with hot water until a small test of the washings, collected in a test tube and acidified with nitric acid, only shows a faint cloudiness when silver nitrate is added. Evaporate the filtrate to about 75 cubic centimeters, remove it from the flame, add a few drops of pure ammonia, and then a strong solution of pure ammonium carbonate as long as a precipitate forms. Stir well and allow the precipitate to settle. Filter, receiving the filtrate in a porcelain dish, and wash with hot water rendered faintly alkaline with ammonia until the washings come through free from chlorine.

Sometimes a very little ammonium carbonate is also added to the wash water. Add a few drops of hydrochloric acid to the filtrate, evaporate to a small bulk, and transfer to a small platinum dish, washing in the last portions with a little

distilled water. Evaporate to dryness on a water bath, and, after heating gently to expel all water, increase the temperature to drive off ammonium compounds, finally heating the dish to very faint redness. When cool, dissolve the residue in a little water, add a drop or two of ammonia, then a few drops of ammonium carbonate, and heat on the water bath for a few minutes. Filter, and wash with water rendered faintly alkaline with ammonia, receiving the filtrate in a small, weighed, platinum dish. Acidulate the filtrate with a few drops of hydrochloric acid, evaporate to dryness on the water bath, then place the dish in an air bath and raise the temperature from 100° to about 140° . Remove the dish from the air bath, and heat it cautiously over a burner, to expel ammonium salts, finally heating the dish until it shows a faint red tinge. Cool in a desiccator, and weigh as soon as cool. The weight of the combined chlorides of sodium and potassium is thus obtained.

Dissolve the residue in a few cubic centimeters of water, add a nearly neutral solution of platinum chloride in sufficient quantity to convert the chlorides of sodium and potassium into the corresponding double chlorides of platinum and these metals, and have a moderate excess remaining. Place the dish on a water bath in which the water is maintained at as near the boiling point as possible, and evaporate the contents to a pasty consistency. Add 35 cubic centimeters of 80-per-cent. alcohol, and stand the dish in a warm place for an hour, stirring the contents occasionally to dissolve the double chloride of sodium and platinum. Filter on a weighed paper, wash thoroughly, but not excessively, with 80-per-cent. alcohol, dry in an air bath at 130° until a constant weight is obtained, and weigh as potassium-platinum chloride K_2PtCl_6 .

From the weight of potassium-platinum chloride obtained, calculate the weight of potassium chloride, and subtract this from the weight of the mixed chlorides. The remainder is the weight of sodium chloride. Calculate the sodium and potassium to the oxides, Na_2O and K_2O , and report them as such.

EXAMINATION OF WATER

PRELIMINARY REMARKS

10. The process of analysis to be pursued in the examination of water depends on the purpose for which the water is to be used. It is most frequently analyzed to determine its fitness for drinking or culinary purposes, or as a boiler supply. As the fitness of a water for these two purposes depends on entirely different conditions, a water that would be well adapted to one purpose might be absolutely unfit for the other. The subject is therefore usually divided into the analysis of potable water, and the analysis of water for boiler supply, and this division of the subject will be observed in the present work. A chemist is occasionally called on to determine the fitness of a water for some particular manufacturing process, and, although we cannot treat every possible case, the student that masters what is given here will be able to answer all such questions for the determinations necessary, and the methods of making them will readily suggest themselves.

There are several methods of reporting the results of water analyses. The oldest method, and one that is still very largely employed, is to report the amount of each constituent in grains per gallon. This method is likely to cause confusion, as there are several gallons having different capacities. The English Imperial gallon contains 70,000 grains, and the United States gallon contains 58,318 grains. By far the most rational method of reporting results, is in parts per million, or, what is the same thing, in milligrams per liter, or to report them in parts per hundred thousand. If results are reported in parts per million, or milligrams per liter, they can readily be changed to grains per gallon, if desired, by means of a very simple calculation. One liter of

water contains 1,000,000 milligrams, and one U. S. gallon contains 58,318 grains. Hence, the number of milligrams in a liter of a constituent, multiplied by 58,318, and the result divided by 1,000,000, gives the number of grains of that constituent in a U. S. gallon of the water. If this method of reporting results is adopted, it should always be stated in the report that the U. S. gallon is used.

POTABLE WATER

11. The principal determinations usually made to determine the fitness of a water for drinking and cooking purposes are: chlorine; free and albuminoid ammonia; oxygen consumed in the moist combustion process; and nitrates, nitrites, and poisonous metals. In addition to these, the total solids and the hardness are frequently determined.

It is difficult to say how much of any one of these constituents may be found in a water without condemning it, but each furnishes valuable indications, and, taken together, give a fairly good idea of the purity of the water. Obviously, impurities coming from some sources are much more injurious than if coming from others. Thus, the organic matter coming from sewage would be more injurious than the same quantity coming from vegetable matter, and, in giving an opinion as to the quality of a water, a chemist must use his judgment. If possible, the chemist should select the sample himself, in order that he may examine the surroundings, and see from what sources pollution may come. In many cases, this will aid him materially in forming an opinion in regard to the quality of the water, for, if the water is found to contain a small amount of impurity, he will know whether it is likely to be dangerous or not.

12. Collecting a Sample.—The amount of water to be collected as a sample will depend on circumstances, but in no case should less than about 2.5 liters be taken. It is best to collect and preserve the sample in a large glass-stoppered bottle. A 5-liter bottle with a ground-glass stopper

is very handy for this purpose, but in the absence of such a bottle, a large bottle, or demijohn, with a new, clean cork stopper may be used. Too great stress cannot be laid on the fact that in collecting samples and analyzing the water, strict cleanliness is absolutely essential. The reason will be obvious when the student considers that in most cases only fractions of 1 part in a million are sought. The best method of preparing the bottle for the reception of the sample is to pour in a little strong sulphuric acid, and cause it to flow over the entire inner surface of the bottle, then pour most of it out, and wash the bottle with pure water, continuing to rinse it for some time after the washings have ceased to show a trace of the acid. Then, before collecting the sample, the bottle should be thoroughly rinsed out with some of the same water that is to be analyzed. Then fill the bottle completely and empty it. This is to drive out any gaseous substances that may remain in a bottle.

In taking a sample from a river or pond, care should be taken to avoid scum or other matter floating on the surface. The bottle should be immersed at some distance from the shore, and held under the water until entirely full. A sample of river water should be taken near the middle of the stream. In examining a city supply, it is best to draw the sample from the street mains, and, in examining the water supplied to a house, the water is drawn from a faucet, in the usual manner. To obtain a fair sample in such cases, the water should be allowed to run a short time before taking the sample, in order to avoid collecting the water that has been standing in the pipes for some time.

In any case, the bottle should be nearly, but not quite, filled with the water; the stopper should be inserted at once, and a piece of clean linen cloth drawn over it tightly and tied in place. Never use sealing wax over the stopper. If it is desired to seal the bottle, seal the ends of the string that holds the cloth. The sample should be kept in a cool dark place, and the examination should take place as soon as convenient after the sample is taken. At all events, the analysis should be made within 48 hours if possible.

TOTAL SOLIDS

13. The total amount of solid matter in a sample of water was at one time considered a very important indication of its quality, but, at present, it is not regarded as very important, and is frequently omitted. As the determination is very simple, and indications of greater or less value are obtained in this way, it should usually be made. The details of the process are as follows:

14. Determination of Total Solids.—Make a water bath by filling a rather tall beaker to about half its capacity with distilled water, placing it on a gauze over a Bunsen burner, and heating it to boiling. On this, place a perfectly clean platinum dish of convenient size to be weighed (one weighing about 50 grams is a good size), and heat it for a few minutes. Remove it from the water bath, wipe the water from the outside of the dish with a clean dry cloth, heat it in an air bath at exactly 105° for 10 minutes, transfer to a desiccator, and weigh as soon as cool.

After weighing the dish, place it on the water bath again, and pour into it 100 cubic centimeters of the water to be analyzed. As a rule, the dish employed will not hold this amount, and the water must be added in successive portions. In this case, measure out 100 cubic centimeters of the water, add enough of it to fill the dish to about three-fourths its capacity, and stand the rest aside, keeping it covered to protect it from dust. When about two-thirds of the water in the dish has evaporated, add the remainder, and evaporate to dryness. Leave the dish on the bath 10 or 15 minutes after the residue appears dry, to expel the last traces of moisture; then remove it, wipe the outside with a clean soft cloth, transfer to the air bath, and keep at exactly 105° for 30 minutes; place it in a desiccator, and weigh as soon as cool. As 100 cubic centimeters (.1 liter) of the water was taken for this determination, the weight in milligrams of the residue multiplied by 10 gives the milligrams of total solids in a liter of the water, or, what is the same thing, the parts per million.

Many chemists prefer to stand the dish on a cold, clean porcelain slab to cool, but as the residues from many samples of water contain deliquescent substances, and, therefore, rapidly increase in weight when allowed to stand in the air, it is always best to cool the dish in a desiccator; and, in every case, the dish should be weighed quickly, as soon as it is cold.

15. Examination of the Residue.—Formerly, it was the custom to ignite the residue, weigh again, and call the loss *organic matter*, and the results thus obtained were considered very significant. It is now known that the loss in weight during this operation is, in most cases, principally due to other constituents, and the results thus obtained are utterly valueless as far as their original purpose is concerned. Having the solid residue, however, it is well to make a slight examination of it as follows:

Remove a portion of it to another dish, and add a few drops of hydrochloric acid. If effervescence occurs, it shows the presence of a carbonate, probably of calcium. Pour the solution into a test tube, render it alkaline with ammonia, and see if it remains clear. Then add a few drops of ammonium oxalate, and heat the solution. The formation of a white precipitate shows the presence of calcium, which, taken together with the effervescence, proves that the water contains calcium carbonate, which is found in all the water in limestone districts, and is comparatively harmless.

Cautiously heat the dish containing the remainder of the residue over a Bunsen burner, and note any change in the appearance of the residue, and any odor that may be given off. The heat should be applied very gently at first, and the temperature raised gradually, until the dish becomes red. If the residue becomes dark-colored, organic matter is indicated, and the amount of organic matter present may be roughly surmised from the depth of the color developed. Organic matter, as a rule, also emits an odor when burned, and this should be noted.

The amount of solid matter permissible in a water to be used for domestic purposes depends, of course, on the

character of the solids; hence, this determination taken alone is of but little value in determining the quality of a water. If, however, the residue is examined as directed, something more of the character of the water is indicated, and, when the results of this determination are considered together with those of the other determinations to be made, they help to form an opinion as to the quality of the water. The water may contain considerable mineral matter of a harmless nature and still be a very good water for domestic use. Many very good drinking waters contain as much as 300 or 400 milligrams of total solids per liter, and, unless the sample contains more than 500 milligrams of solid matter, it should not be condemned for domestic use for this reason alone.

CHLORINE

16. Determination of Chlorine.—In determining the chlorine in water, we avail ourselves of the well known relation between silver, chlorine, and chromic acid. When a solution of silver is added to a solution containing both a chloride and a chromate, the silver unites with the chlorine until it is all precipitated as white silver chloride, and then begins to unite with the chromic acid, forming red silver chromate. The details of the process are as follows:

Measure 100 cubic centimeters of the water into a clean porcelain dish, add a few drops of potassium-chromate solution, and titrate with a standard solution of silver nitrate. As each drop of the silver solution falls into the water, it produces a red color at the point of contact, owing to the fact that all the chlorine in this part of the water is precipitated, and the silver left over unites with chromic acid, forming red silver chromate. On stirring, this precipitate comes in contact with more chlorine, which immediately takes the silver from the chromic acid, and forms white silver chloride, thus destroying the color. This goes on until all the chlorine is precipitated as silver chloride, when an additional drop of silver nitrate will give the solution a permanent reddish color, showing that the reaction is complete. From the

quantity of silver solution used, calculate the amount of chlorine in 100 cubic centimeters of the water. This result multiplied by 10 gives the amount of chlorine in a liter. This amount of chlorine in milligrams is, of course, parts per million.

Some chemists prefer to evaporate 1 liter of the water to a small bulk before titrating, and this is a good plan, in order to check the results, when the water only contains a very little chlorine. It is also a good plan to add more of the potassium-chromate indicator, and then another drop of the silver solution, after the reaction is complete, to see if a marked increase in the red color occurs. Neither of these checks can be considered essential, however, for the writer has repeatedly checked analyses without obtaining results that differed appreciably.

17. Significance of Chlorine.—Chlorine generally exists in water combined with sodium in the form of common salt, and, as this is an article that we require, and take into the system daily, it matters little whether it is taken with our food or in the water we drink; hence, chlorine in itself, unless the amount is excessive, is no cause for rejecting a water for domestic use. Probably too much stress has been laid on the determination of chlorine in drinking water; and water that was organically pure, and of very good quality for domestic use, has been rejected on account of the chlorine it contained. This is an important determination, however, when the results are considered in connection with those obtained in the other determinations, and are intelligently interpreted. A little consideration of the matter will show how they may be of use. The water in regions remote from salt deposits frequently contains but a mere trace of chlorine, while sewage is always heavily charged with this element; hence, any considerable quantity of chlorine in a water has come to be regarded as an indication of sewage contamination.

A water containing a marked increase in chlorine over the amount usually found in the locality from which the water

comes, should certainly be regarded with suspicion. This determination is important in the examination of samples of water suspected of sewage contamination during an epidemic, on account of the rapidity with which results may be obtained. In such cases, if a water is found to contain a considerable quantity of chlorine, its use should be suspended at once, pending a further examination. It must always be borne in mind that a water may be heavily charged with organic matter of vegetable origin, and still contain but very little chlorine, and, consequently, freedom from chlorine is no sign that water is free from organic matter of vegetable origin, and this is, of course, to be avoided. Sewage contamination is regarded as more dangerous than the same amount of vegetable matter, and the amount of chlorine in a water may help us to decide whether the contamination is of animal or vegetable origin, and may thus help us to discover the source of pollution.

It is impossible to say how much chlorine a water may contain without being suspected of sewage contamination, for the normal quantity of chlorine varies greatly in different sections of the country; but when the normal quantity in any locality has been established, any increase over this amount should be regarded with suspicion. The writer has analyzed samples of water containing less than 1 part per million of chlorine, while near the coast or in the vicinity of salt deposits, water that is perfectly wholesome may contain more than 20 parts per million of this element.

SOLUTIONS FOR CHLORINE DETERMINATION

18. Silver Nitrate.—The silver-nitrate solution for this purpose is usually made of such strength that 1 cubic centimeter of it will precipitate exactly 1 milligram of chlorine. It is made up as follows: Weigh out exactly 4.79 grams of the pure, dry silver-nitrate crystals; transfer this to a graduated liter flask, dissolve it in pure distilled water, and dilute the solution to exactly 1 liter. As silver nitrate is weighable, this solution will be of such strength that 1 cubic

centimeter of it will precipitate exactly 1 milligram of chlorine, if the pure salt is used, but it is best to check it by running it against a sodium-chloride solution of known strength. To make this solution, dissolve 1.65 grams of pure, dry sodium chloride in water, dilute to 1 liter, and mix thoroughly, using distilled water that is free from chlorine, of course. Each cubic centimeter of this solution contains exactly 1 milligram of chlorine, and, therefore, should exactly match the silver solution. This solution is sometimes handy in making the determinations. After taking the burette reading when titrating, a few more drops of the silver solution may be added, to produce a deep-red color; this may be destroyed with a measured quantity of the salt solution, and silver nitrate again added until the reaction is complete. Then, by subtracting the amount of sodium chloride added from the total quantity of silver nitrate used, a check on the determination is obtained.

19. Potassium Chromate.—The solution of potassium chromate used as indicator is usually a cold saturated solution of the pure salt in pure water. The solution may be made up by dissolving about 20 grams of the pure salt in 100 cubic centimeters of water. Both the potassium chromate and the water used in making up this solution must be absolutely free from chlorine. Of course, this applies with equal force to the materials used in making up the other solutions for this determination.

THE AMMONIA PROCESS

20. The determination of total solids and chlorine gives us indications that are valuable in throwing light on the subject when considered in connection with other results, but are of little value in themselves. We now come to the determination of organic matter, and the results obtained are usually sufficient in themselves to establish the character of the water. The ammonia process is divided into two parts, the determination of *free ammonia* and of *albuminoid*

ammonia. The process depends on the fact that when a sample of water is boiled with sodium carbonate, the free ammonia (which term includes ammonium salts) dissolved in it is expelled, and passes off with the first part of the water as it is evaporated. Now, having the water free of uncombined ammonia and ammonium salts, if potassium permanganate and a large excess of potassium hydrate are added and the boiling continued, the nitrogenous organic matter is decomposed, yielding a quantity of ammonia proportional to the amount of such matter contained in the water. The ammonia is collected in the distillate, and its quantity determined by means of the very delicate Nessler reagent. The determination of the ammonia is one of the most important, if not the most important, of the determinations made in the examination of water for domestic use. The details of the process are as follows:

21. Free Ammonia.—Choose a tubulated retort that will hold from 1.5 to 2 liters, and provided with a ground-glass stopper; cleanse it thoroughly by rinsing it out, first

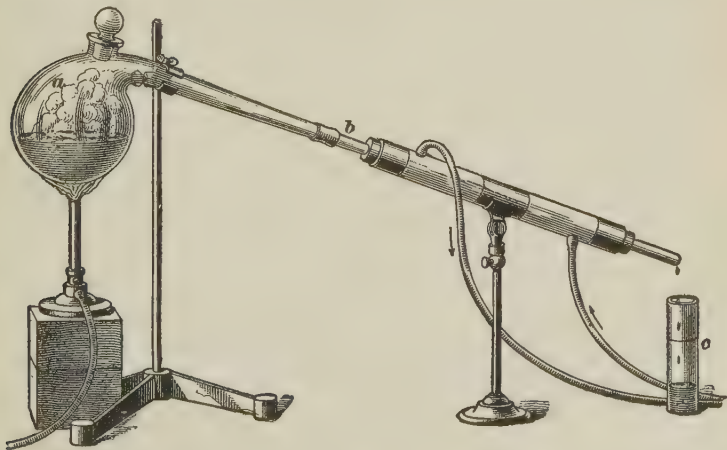


FIG. 1

with strong sulphuric acid, and then washing until the washings contain no acid, finally with distilled water, and fix it in the clamp on a retort stand, as shown at *a*, Fig. 1. Fit

the neck of the retort into the tube of a Liebig condenser, wind it tightly with a piece of thin flexible rubber, and bind this in place by means of a cord, as shown at *b*, thus securing a perfectly tight connection. Under the end of the condenser tube, stand the Nessler cylinder *c* to collect the distillate. From half a dozen to a dozen Nessler tubes will be required for the determination. They should be made of thin colorless glass, and must be of uniform size and form. Cylinders of a little more than 100 cubic centimeters capacity are probably the most convenient; each should have a mark on the side to show when 50 cubic centimeters of distillate have been collected, and they should be so nearly of the same size that these marks will all come within one-sixteenth of an inch of one another. The bottoms of the tubes should be perfectly flat, so that they will stand firmly on the working bench or table. The arrangement of the apparatus will be understood from Fig. 1.

When all is in readiness, measure 200 cubic centimeters of absolute water into the retort, add 10 cubic centimeters of sodium-carbonate solution, drop in five or six small glass balls, to prevent bumping, and close the retort with the ground-glass stopper, which must be scrupulously clean. Place a good Bunsen burner under the retort, so that the flame plays directly on it, but take care not to allow the flame to strike the glass above the water line. When 50 cubic centimeters of distillate have passed over, remove the Nessler cylinder, and place a clean one in its place, to collect the next 50 cubic centimeters of distillate passing over. When 100 cubic centimeters have passed over, remove the light from the retort. This will remove any ammonia that remained in the retort, or that may have been introduced with the sodium carbonate, and the 100 cubic centimeters of water and sodium carbonate, as well as the retort itself, are now perfectly free from ammonia. It is well to test the two distillates collected, with Nessler reagent, to learn if there was any ammonia to start with.

Now measure 500 cubic centimeters of the water to be examined into the retort, stopper it tightly, return the

burner to its position, and so regulate the flame that about 50 cubic centimeters of distillate will collect every 15 minutes. If the distillation is carried on much more rapidly than this, some ammonia will escape. While the first 50 cubic centimeters of distillate are collecting, measure different quantities of standard ammonia solution into several Nessler cylinders, and dilute each to 50 cubic centimeters with absolute water. It is handy to have such standards ranging from .005 to .05 milligram of ammonia in the 50 cubic centimeters of water. When the first cylinder is filled to the 50-cubic-centimeter mark, remove it, and stand a clean cylinder in its place, to collect the next 50 cubic centimeters of distillate passing over. By means of a 2-cubic-centimeter pipette, drop exactly 2 cubic centimeters of Nessler reagent into each of the standards and the 50 cubic centimeters of distillate, and stir each up. Allow the tubes to stand 5 minutes after adding the Nessler reagent and stirring. The reddish-brown color will by this time be developed and is fairly constant, so that one set of standards may be used for a series of determinations. The standards are made up only once a day. Have the cylinders standing on a white surface, and, by looking down through them, compare the colors and match the sample with a standard. If the sample has a color differing from that of any of the standards, a very close estimate of the amount of ammonia it contains may be made. In this case, quickly make up two more standards containing very nearly the estimated amount of ammonia, add 2 cubic centimeters of Nessler reagent to each, and, after allowing them to stand about 5 minutes, compare the sample with these standards.

When a standard is obtained, the color of which exactly matches that of the distillate, we know that each contains the same quantity of ammonia, and as the amount of ammonia in the standard is known, we thus learn the quantity in the distillate. If the distillate contains more ammonia than any of the standards, it may be diluted to 100 cubic centimeters, stirred well, half of the solution poured out, 1 cubic centimeter of Nessler

reagent added to the portion remaining in the tube to make the quantity of Nessler reagent in each tube the same, and the colors again compared. But under no circumstances must ammonia be added to a solution after the Nessler reagent has been added, for this is almost certain to give erroneous results. The free ammonia will frequently all pass over in the first three portions of distillate, and it is very seldom that any remains after the fourth, but, for the sake of uniformity, five portions of distillate, of 50 cubic centimeters each, should always be collected and Nesslerized, just as was done with the first portion. By adding the results obtained in Nesslerizing the five portions of distillate, the amount of free ammonia in 500 cubic centimeters of the water is obtained, and the result thus obtained in milligrams, multiplied by 2, gives the number of parts of free ammonia in a million parts of water.

22. Albuminoid Ammonia.—The free and the albuminoid ammonia are determined in the same sample. When 250 cubic centimeters of the water have passed over and been Nesslerized for free ammonia, remove the burner for a few moments, add 50 cubic centimeters of a solution of potassium hydrate and potassium permanganate, return the burner to its place, and continue the distillation. Collect the distillate in portions of 50 cubic centimeters each, and Nesslerize just as in the determination of free ammonia, continuing the operation as long as a distillate gives a reaction with Nessler reagent. The total amount of ammonia found in this way after the potassium hydrate and permanganate solution is added, is the albuminoid ammonia formed by the decomposition of the nitrogenous organic matter in 500 cubic centimeters of the water, and this amount in milligrams, multiplied by 2, gives the albuminoid ammonia in the water in terms of milligrams per liter or parts per million.

In laboratories where many water analyses are made, the very handy form of apparatus shown in Fig. 2 is largely used for this process. The flask *a* has a capacity of about 2 liters; it is provided with a ground-glass stopper that fits

perfectly, and has a side neck tube that is bent to point straight downwards when the flask is held in the clamp *b* over the burner *c*. The side neck tube is connected with the zigzag tube passing through the vertical condenser *d*, and the Nessler cylinders are held in the rack *e* in such a way that they pass successively under the zigzag tube to receive the

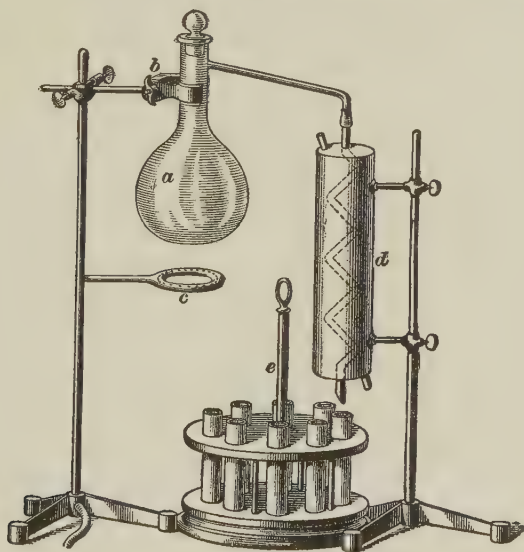


FIG. 2

distillate when the rack is revolved. When using this apparatus, measure the sample into the flask *a*, insert the stopper tightly, light the burner *c*, and proceed with the determination exactly as when a retort is used.

23. Significance of Ammonia.—Nearly all natural waters contain minute quantities of free ammonia, and this in itself is not injurious; but an increase in the amount of this constituent points to unhealthy conditions. It has been suggested that free ammonia is produced in water by the breaking up of albuminous matter before the water is examined, thus indicating that the water is undergoing purification, but that it is not yet sufficiently pure for

domestic use. Water that is contaminated with urine yields a relatively large amount of free ammonia. For this reason, it is sometimes spoken of as *ureal* ammonia, and is regarded as an indication that the water is polluted with sewage. It is the writer's experience, however, that free ammonia sometimes comes from other sources. The amount of free ammonia in water varies with the source. It is usually greater in wells than in streams or ponds. Chemists differ as to the amount that may be present without danger to health. It may be stated, however, that water from a stream or pond containing more than .1 part per million should never be used, and, to be considered as very pure, it should contain considerably less than this.

Although chemists differ somewhat in regard to the significance of free ammonia, they all agree that a relatively large amount of albuminoid ammonia indicates a very dangerous condition, and that a water yielding a very large amount of this constituent should be condemned without qualification. The albuminous matter in water may be either of animal or vegetable origin. The former is regarded as the most dangerous, but the latter, if present in excessive quantity, is almost certain to cause disease. If familiar with the surroundings, the character of the organic matter in a sample of water may be inferred from its source. Another indication is obtained when the water is distilled in the determination of ammonia. The albuminoid ammonia derived from animal matter usually comes over more rapidly and regularly than that from vegetable matter. Much may also be inferred from the results of the other determinations. Water containing vegetable matter alone is frequently almost free from chlorine and free ammonia, while the albuminoid ammonia is relatively high. On the other hand, water polluted with sewage always contains an increased amount of chlorine, and, generally, free ammonia also. Wanklyn, who devised this process, says that the albuminoid ammonia should never exceed .15 part per million, and this limit undoubtedly holds in the case of wells and other waters that may contain sewage contamination.

Chemists are at present inclined to allow a little more in the case of streams and ponds in thickly wooded districts, where the organic impurity consists principally of dead leaves; but, in this case, the water should not contain more than .35 part per million of albuminoid ammonia. In any case, it should be remembered that in order to be regarded as very pure, the water should contain considerably less than these figures given as limits.

SOLUTIONS FOR THE AMMONIA PROCESS

24. Absolute Water.—Ordinary distilled water cannot be used in making the solutions used in the ammonia process, for it contains enough ammonia to render it useless for this purpose, and ammonia-free water, known as absolute water, must be prepared. The best way to do this, is to make use of the fact that when water is distilled, the free ammonia all passes over with the first third of the distillate, the second third of the distillate is free from ammonia, and the last third contains the remainder of the ammonia. Place a convenient quantity—say 15 liters—of good drinking water in a distilling apparatus and apply heat. Discard the first 5 liters of distillate, then test a little of the distillate with Nessler reagent, and, if it is free from ammonia, collect the next 5 liters, and then stop the distillation. The portion collected will be free from ammonia, and is known as absolute water. The first portion passing over should not be thrown away, as it is sufficiently pure for ordinary use as distilled water. The portion remaining in the distilling apparatus should be thrown out, however, and the apparatus should be rinsed out with fresh water. The absolute water should be kept in glass-stoppered bottles, and it is best to cover the tips with caps to prevent the deposition on them of ammonium compounds from the air of the laboratory. It should be used within a reasonable time after it is prepared, for after standing a long time in the bottles, it will give a cloudy solution when Nessler reagent is added, and is therefore useless for this purpose.

25. Sodium Carbonate.—This solution is made by dissolving 50 grams of pure sodium carbonate in 250 cubic centimeters of absolute water. It should be kept in a bottle with a ground-glass stopper, but care must be taken to keep the stopper from sticking. The object of the solution is to expel any so called free ammonia that is combined with an acid. Its use would not be necessary in many cases, but, for the sake of uniformity, it should be added to every sample. It may be stated here that perfect uniformity of conditions is essential for success in water analysis.

26. Nessler Reagent.—Dissolve 15 grams of mercuric chloride in about 500 cubic centimeters of absolute water. Dissolve 35 grams of potassium iodide in about 200 cubic centimeters of absolute water. Pour the first solution into the second, until a faint, permanent, red precipitate begins to form, adding the mercuric chloride cautiously towards the last. The solution at this point should contain a very slight red precipitate that does not redissolve, even upon vigorous stirring. It now remains to make it strongly alkaline, and to render it sensitive. To do this, add 160 grams of pure solid potassium hydrate, and when it has dissolved and the solution has cooled, dilute it to 1 liter with absolute water, and mix it thoroughly. If potassium hydrate is not at hand, 120 grams of pure sodium hydrate may be substituted for it. The slight reddish precipitate in the solution will be dissolved by the potassium hydrate, and more mercuric chloride must now be added to render the solution sensitive. A cold saturated solution in absolute water is used. Add it cautiously until the last drop added produces a permanent precipitate, and allow this to settle. The clear supernatant liquid should now have a slight yellowish tint, and, if colorless, it is never sensitive. In this case, a little more mercuric chloride must be added, and, after being thoroughly mixed, the solution must be allowed to settle again.

The solution should next be tested to ascertain its condition. For this purpose, measure a quantity of the dilute standard

ammonia solution, containing .01 milligram of ammonia, into a Nessler cylinder; dilute it to 50 cubic centimeters with absolute water, and add 2 cubic centimeters of the solution to be tested. If it is sufficiently sensitive, a yellowish-brown tint will be imparted to the solution in the Nessler cylinder almost immediately. If a distinct color is not developed in the course of half a minute, the solution is not sufficiently sensitive. In this case, add more mercuric chloride, mix thoroughly, allow it to settle, and test again. The stock of Nessler reagent should be kept in a tightly stoppered bottle, and, from time to time, small quantities of it are poured into a small bottle, from which it is drawn as it is used.

27. Standard Solution of Ammonia.—A dilute solution of ammonium chloride is used as a standard in Nesslerizing. It is made up as follows: Dissolve 3.14 grams of pure ammonium chloride in absolute water, dilute to exactly 1 liter with absolute water, and mix the solution thoroughly. This solution is of such strength that 1 cubic centimeter of it contains 1 milligram of ammonia NH_3 , and is therefore much too strong for use in Nesslerizing. By means of a burette, measure exactly 10 cubic centimeters of this solution into a liter flask, dilute it to the mark with absolute water, and mix it thoroughly. This solution contains .01 milligram of ammonia in 1 cubic centimeter, and is therefore of a convenient strength to use in Nesslerizing. This solution should be kept in a glass-stoppered bottle, the lip of which is protected from ammonium compounds in the air by means of a cap. In examining extremely bad waters, it is sometimes handy to have a stronger standard solution of ammonia. Such a solution is made by diluting 100 cubic centimeters of the strong solution first made up to 1 liter. This solution will be of such strength that 1 cubic centimeter of it contains .1 milligram of ammonia.

28. Potassium Hydrate and Permanganate.—This solution, which is used to decompose the nitrogenous organic

matter, and set free the albuminoid ammonia, is made as follows: Dissolve 8 grams of pure crystallized potassium permanganate and 200 grams of potassium hydrate in 1 liter of distilled water. Boil the solution until about one-fifth of it has evaporated, and add sufficient absolute water to bring the volume of the solution up to 1 liter when it is cold. Keep the solution in a glass-stoppered bottle, and, when not using it, move the stopper every few days, to keep it from sticking. This solution must always have the reddish-violet color of permanganate. If it becomes green, either in the stock bottle or in the retort when in use, no reliable results can be obtained with it, and a fresh solution must be made up.

29. Practical Suggestions.—If many analyses of water are made, it is best to set apart a portion of the laboratory for this purpose exclusively, and to keep it as free from fumes as possible. The ammonia process cannot be carried out successfully in a laboratory filled with ammonia fumes. It is best to keep the apparatus used in the ammonia process for that purpose alone. At all events, it should not come in contact with organic matter. The apparatus must be thoroughly cleaned before it is used. It is not sufficient to clean it before putting it away, and then to use it without a second washing, for ammonium compounds from the air may be deposited in sufficient quantity to vitiate the results. It is not usually necessary to employ distilled water in washing the apparatus. If washed with a large quantity of good tap water and allowed to drain, it will be perfectly clean; and, under no circumstances, should apparatus used in water analysis be wiped with a cloth.

THE MOIST COMBUSTION PROCESS

30. Before the ammonia process came into general use, chemists tried to estimate the amount of organic matter in water by the amount of oxygen required to oxidize it, using potassium permanganate to supply the oxygen. The methods employed were rather crude, and the results obtained were

unsatisfactory, as, in many cases, only a small fraction of the organic matter was oxidized. At present, the so called moist combustion process is largely used, and it is believed that by this method the organic matter in a water is oxidized, and the amount of oxygen used may be accurately measured. It has been objected to this process that when two samples are treated, one of which contains vegetable matter, and the other an equal amount of animal matter, the water containing the vegetable matter will consume the larger quantity of oxygen, while that containing the animal matter is undoubtedly the more dangerous.

While the results obtained by this method are probably not so important as those obtained by the ammonia process, they are of value inasmuch as they give a further idea of the amount of organic matter in a sample, and also of its character. It has been stated that the weight of organic matter in a liter of water is approximately equal to the weight of oxygen consumed when a liter of the water is subjected to the moist combustion process. While this statement is correct when the organic matter is starch and some other compounds, it will not hold good in all cases, and, consequently, the results should be stated in milligrams of oxygen consumed, without attempting to state the weight of organic matter present.

The amount of oxygen that may be consumed by the carbonaceous matter in a liter of water without rejecting it for domestic use, is not so clearly defined as in the case of ammonia. In fact, the results obtained by this process are more largely used to throw light on the results of the ammonia process than to establish the quality of the water, when considered by themselves. It may be stated, however, that to be considered of first-class quality, a liter of the water should not consume much more than 1 milligram of oxygen. Many drinking waters that are considered wholesome consume from 1 to 3 parts of oxygen per million, but anything above this should be regarded with suspicion, and a water, 1 liter of which consumes more than 5 milligrams of oxygen, should usually be rejected. The details of the process are as follows:

31. Determination of Oxygen Consumed.—Mix in a flask 200 cubic centimeters of the water to be examined with 10 cubic centimeters of the dilute sulphuric acid. Heat rapidly until the water is just about to boil, and run in from a burette the standard potassium-permanganate solution until the water has a decided red color. Boil 10 minutes, watching carefully and adding more permanganate as the color fades. Do not allow the color to fade nearly out before adding more permanganate; but add the permanganate so as to keep the color constant. Remove the lamp, and add from another burette sufficient standard oxalic-acid solution to destroy the color; 10 cubic centimeters is generally the right amount. Then add the permanganate until a faint pink color again appears. From the total amount of permanganate used deduct that corresponding to the oxalic acid used, and from the remainder calculate the number of milligrams of oxygen consumed by the 200 cubic centimeters of water. This multiplied by 5 will give the number of milligrams consumed per liter.

32. In case the water contains nitrites, ferrous salts, or hydrogen sulphide, corrections for these substances, which also reduce permanganate, must be made.

SOLUTIONS REQUIRED

33. Standard Potassium Permanganate.—Dissolve .395 potassium permanganate in distilled water, and dilute to 1 liter. Each cubic centimeter of this solution contains .0001 gram available oxygen. The available oxygen in the presence of sulphuric acid and easily oxidized substances may be represented by the equation:



34. Standard Oxalic Acid.—Dissolve .7875 gram pure oxalic acid $C_2H_2O_4 \cdot 2H_2O$ in distilled water and dilute to

1 liter. This solution if titrated with the permanganate solution while hot and acid with sulphuric acid should correspond with it cubic centimeter for cubic centimeter. The solution, however, does not keep well, and in practice it is necessary to standardize the solution by adding 10 cubic centimeters of the oxalic acid to 200 cubic centimeters of distilled water and 10 cubic centimeters of the dilute sulphuric acid. This is heated to boiling and titrated by the standard permanganate solution. From the number of cubic centimeters of permanganate used the value of the oxalic acid is calculated. This standardizing should always be done the same day a determination is made.

35. Dilute Sulphuric Acid.—Mix 1 volume of pure concentrate sulphuric acid with 3 volumes of distilled water and drop in sufficient permanganate solution to give a very faint pink color. Heat to 60° C., and keep at that temperature 2 hours. If the color disappears, add more permanganate until it leaves the solution a very faint pink after heating 2 hours to 60° C.

NITROGEN AS NITRITE

36. It is generally admitted that nitrites found in pond or river water ordinarily come from the putrefaction of nitrogenous organic matter—usually of animal matter. In deep wells, the conditions are somewhat different. These waters may contain nitrites that have been formed by the deoxidation of nitrates in percolating through strata containing mineral reducing agents.

37. Professor Mallet considers this determination of great importance, and the writer's experience agrees perfectly with this view. At all events, the result of this determination should be kept in mind in deciding the quality of a water, and, when nitrites are present, the results of the other determinations should be interpreted with greater strictness than when they are absent. Professor Mallet examined eighteen samples

of water from different sources, all of which were believed to be wholesome, and found that the average of the eighteen samples was .0135 part of nitrogen as nitrite in a million parts of water. He also examined nineteen samples of waters that were thought to have caused disease, and found the average to be .0403 part of nitrogen as nitrite per million. It has been the experience of other authorities that the nitrogen as nitrite found in good wholesome water is usually much less than the figures given above.

38. Determination of Nitrogen as Nitrites.—Place a measured quantity, 50 or 100 cubic centimeters, in a Nessler cylinder, add 1 drop of concentrate hydrochloric acid, 1 cubic centimeter of sulphanilic-acid solution, and 1 cubic centimeter of naphthylamine hydrochloride. Mix thoroughly by stirring with a glass rod, cover with a watch glass, and set aside for 30 minutes. Prepare at the same time standard solutions containing known amounts of standard sodium nitrite diluted to 50 or 100 cubic centimeters with absolute water, and the same amount of reagents as above. At the end of 30 minutes compare the depth of the pink color formed in the water to be tested with the various standard solutions in the same way as in the ammonia determination.

SOLUTION FOR NITROGEN AS NITRITES

39. Sulphanilic Acid.—Dissolve 1 gram of sulphanilic acid in 100 cubic centimeters of hot water, cool, and preserve in a stoppered bottle.

40. Naphthylamine Hydrochloride.—Boil .5 gram of naphthylamine hydrochloride with 100 cubic centimeters of water for 10 minutes, adding water to make good any evaporation. When cool, transfer to a stoppered bottle and preserve in a dark place.

41. Standard Nitrite Solution.—The sodium or potassium nitrite sold by chemical dealers is not pure enough to

be used for this purpose, and, consequently, silver nitrite is employed in its preparation. This salt may be obtained from dealers, but, in order to be sure of its purity, it is best to prepare it. This is done as follows: Make up strong solutions of silver nitrate and sodium or potassium nitrite, using a very little more of the nitrite than the calculation would indicate as necessary. Heat both solutions just to the boiling point, mix them, and filter at once. The silver nitrite formed dissolves quite readily in boiling water, but crystallizes from the filtrate as it cools. When quite cold, pour off the mother liquor, wash the crystals once by decantation with a little cold water, dissolve them in a little boiling water, filter and recrystallize. Wash these crystals once by decantation with a little cold water, drain this off and dry them, at first over a water bath, and, finally, in a desiccator. When dry, the crystals will consist of pure silver nitrite, 11 grams of which contain 1 gram of nitrogen. The salt must not be exposed to a strong light, either during or after preparation. Continued boiling must also be avoided, as this tends to slowly decompose the silver nitrite with the formation of nitrate.

Weigh out .275 gram of the pure silver nitrite, dissolve it in a little hot water, and add a slight excess of sodium-chloride solution. This will precipitate the silver as chloride, and form a corresponding amount of sodium nitrite. Filter off the silver chloride, wash the precipitate with absolute water until the filtrate and washings amount to exactly 250 cubic centimeters, and mix this solution thoroughly. Measure out exactly 10 cubic centimeters of this solution, dilute it to 1 liter, mix it thoroughly, and keep it in a tightly stoppered bottle. The liter of solution contains 1 milligram of nitrogen in the form of nitrite, and, consequently, each cubic centimeter contains .001 milligram of nitrogen.

42. In comparing colors, if 100 cubic centimeters of water are taken, and its color is found to match that of the solution in the cylinder containing 3 cubic centimeters of the standard nitrite solution, it shows that 100 cubic centimeters

of the water contain .003 milligram of nitrogen, and that 1 liter contains .03 milligram of nitrogen as nitrite. Or, as it is more frequently stated, the water contains .03 part per million of nitrogen as nitrite.

NITROGEN AS NITRATE

43. The nitrates in water are generally believed to come principally from the oxidation of nitrogenous organic matter, and it has been asserted that when the nitrogen reaches this state of oxidation, all danger is past, and the nitrates can only be considered as an evidence of past pollution. Experience does not support this statement, for water containing 5 parts per million of nitrogen as nitrate, though the albuminoid ammonia was low, has been known to cause disease. The amount of nitrogen in the form of nitrate ordinarily present in a water depends on its source. In ponds and streams, the quantity is generally rather less than .2 part per million, while in wells, it sometimes reaches ten times this figure. It is probably safe to say that a well water containing over 3 parts per million should be regarded with suspicion. There are a number of methods for the determination of nitrogen existing as nitrate in water. The one given in this Section is largely used and is very satisfactory.

44. The Picric-Acid Test.—The picric-acid, or the phenol-sulphonic, test depends on the fact that when phenol and sulphuric acid are added to a sample of water, the nitric acid in the water converts a corresponding amount of the phenol into picric acid, and, when an excess of ammonia is added to this, a yellow color is produced, the depth of which depends on the amount of picrate present. By comparing this color with that produced when a solution containing a known quantity of nitrate is similarly treated, the amount of nitrogen existing as nitrate in the water is obtained. The details of the process are as follows: Dissolve .7214 gram of pure potassium nitrate in absolute water, and dilute the solution to exactly 1 liter for a stock standard solution. This

solution is then of such a strength that 1 liter contains 100 milligrams of nitrogen, and, consequently, 1 cubic centimeter contains .1 milligram of nitrogen. When ready to make the determination, measure exactly 10 cubic centimeters of the stock solution into a 100-cubic-centimeter flask, dilute it exactly to the mark, and mix it thoroughly. A solution is thus obtained, 1 cubic centimeter of which contains .01 milligram of nitrogen. Measure 10 cubic centimeters of this diluted solution into a small porcelain dish, and into a similar dish measure 10 cubic centimeters of the water to be tested;* place them side by side on water baths, and evaporate to apparent dryness. As soon as the residues appear to be dry, or even while they appear slightly moist, remove the dishes from the water baths. Heating after the residue is dry is almost sure to cause inaccuracies, for nitric acid is slowly expelled by the heat, and some nitrate may be absorbed by the residue from the products of combustion if a gas flame is used in heating the water.

While the sample and standard are evaporating to dryness, mix 6 drops of concentrate phenol and 30 drops of concentrate sulphuric acid. Several methods of making up a stock solution of this reagent have been proposed, but it is found that much more satisfactory results are obtained by making up a small quantity of it just before it is used. Add about 10 drops of this solution to each dish, taking care to add the same quantity to each. Then, by means of glass rods, spread this solution around so that it moistens every particle of the residue. Add 1 cubic centimeter of concentrate sulphuric acid to each dish, and warm them for 2 or 3 minutes on the water bath. Then remove them, allow them to cool, add 10 cubic centimeters of water to each, stir them up, add 5 cubic centimeters of concentrate ammonia to each, and stir them again, whereupon the color will develop. Rinse the solution from the sample into a Nessler cylinder, dilute it to 50 cubic centimeters, and treat the standard as the colors produced indicate as best.

* Add to each 1 drop of the sodium-carbonate solution used in the ammonia determination.

In many cases it will be sufficient to wash it into a Nessler cylinder, dilute to 100 cubic centimeters, mix well, remove small measured portions to other cylinders, dilute them to 50 cubic centimeters each, and compare the colors with that of the sample. As 10 cubic centimeters of the dilute standard are taken, the 100 cubic centimeters in the Nessler cylinder contains .1 milligram of nitrogen, and 1 cubic centimeter contains .001 milligram. If 9 cubic centimeters of this are required to make a solution that, when diluted to 50 cubic centimeters, matches the color of the standard, it shows that 10 cubic centimeters of the water under examination contain .009 milligram of nitrogen existing in the form of nitrate, and, therefore, 1 liter of the water contains .9 milligram, or the water contains .9 part per million of nitrogen as nitrate. In examining very pure samples of water, it is sometimes necessary to evaporate a larger quantity, in order to get a color that is strong enough for accurate comparison. As much as 50 cubic centimeters is sometimes required.

It has been asserted that this method does not yield accurate results with samples containing much chlorine, and this appears to be true if the reagent is made up in considerable quantity and allowed to stand some time before it is used, and may be true in extreme cases even when a fresh solution is used. We have obtained very accurate results by using a freshly prepared solution even in the presence of a large amount of chlorine, and it is stated by some chemists that when the fresh reagent is employed, chlorine has no effect on the results, even though an excessive amount of it may be present. The nitrogen existing as nitrite does not interfere with this determination, as nitrous acid forms nitroso-phenol, which is colorless in dilute solution.

POISONOUS METALS

45. Probably the poisonous metals most frequently occurring in water are copper, lead, and zinc. They are sometimes found in the natural water in the regions where these metals are mined, and some waters have the power of acting

on lead or copper pipes or fixtures, dissolving these metals; or on galvanized iron pipes or vessels, dissolving zinc. Arsenic and chromium, both of which are poisonous, sometimes occur in water, and iron occurs in small quantities in many waters. This latter element, though not generally considered very poisonous, is, nevertheless, very objectionable when present in considerable quantity. When any of these metals are present, they should not be overlooked. For lead, copper, and iron, very simple colorimetric methods may be used.

46. Lead and Copper.—The method generally employed in determining these metals is due to Miller. It consists in comparing the depth of the colors produced by adding ammonium sulphide to the sample and to a standard solution. The details of the process are as follows: Make up a standard solution of lead nitrate by dissolving 1.599 grams of the pure salt in water and diluting to exactly 1 liter. Each cubic centimeter of this solution will contain 1 milligram of metallic lead. Now measure 100 cubic centimeters of the water to be tested into a Nessler cylinder, add 5 drops of concentrate hydrochloric acid, then 1 cubic centimeter of colorless ammonium sulphide, and stir the solution. Into a similar cylinder, measure a small quantity of the standard lead solution, dilute to 100 cubic centimeters, add 5 drops of concentrate hydrochloric acid, 1 cubic centimeter of colorless ammonium sulphide, stir well, and compare the color produced with that of the sample. Prepare other standards in the same way until one is obtained, the color of which exactly matches the sample. The minute quantity of copper or lead usually contained in water contaminated with these metals, will give the sample a brownish color, due to the formation of the dark sulphide. If the water is rendered alkaline by the addition of the ammonium sulphide, the color may be due to iron; hence, after the color has been obtained, the sample and standard should be rendered distinctly acid with dilute hydrochloric acid, adding the same amount of acid to each. A diminution or disappearance of color in the

sample, when thus treated, indicates that the color is due, either partially or wholly, to iron, the sulphide of which is dissolved by dilute hydrochloric acid.

This method, of course, will not distinguish between copper and lead, but, as both metals are poisonous, this is not usually necessary, and the approximate quantity of the two metals may be estimated as above if both are present. If it is required to know which metal is present, a large quantity of the water must be evaporated to a small bulk, and a qualitative analysis made. If copper alone is found to be present, a standard solution of copper sulphate, containing 1 milligram of metallic copper in a cubic centimeter, is made up, and a colorimetric determination made, just as when the lead solution is used. A standard copper solution for this purpose is made by dissolving 3.927 grams of pure crystallized copper sulphate in distilled water, and making the solution up to 1 liter.

It is sometimes desirable to know the action of a certain water on lead pipe. To learn this, place a piece of bright lead in one vessel, and a piece of dull lead in another; cover them with the water, allow them to stand 24 hours, and then examine each sample for lead as directed above.

47. Iron.—Wanklyn states that good drinking water should not contain more than 3 parts of iron per million. This limit may be rather severe, but it is undoubtedly true that a good drinking water should not contain a large amount of iron. Water to be used in washing white goods, or in dyeing, should also contain but little of this element. To determine iron, acidify a suitable volume (200 to 500 cubic centimeters, according to indications) of the water with aqua regia, evaporate this solution to 100 cubic centimeters, pour it into a Nessler cylinder, and add 2 cubic centimeters of ammonium-sulphocyanide solution. Compare the color thus produced with the colors of standards made by adding measured quantities of standard iron solution to Nessler cylinders, diluting to 100 cubic centimeters with distilled water, and adding 2 cubic centimeters of ammonium sulphocyanide.

To make the standard solution of iron, weigh .1 gram of pure iron into a small beaker, and dissolve it in a little hydrochloric acid; add a few drops of nitric acid, and heat to boiling. Wash this solution into a liter flask, and dilute it to the mark with distilled water that is known to be free from iron. Each cubic centimeter of this solution contains .1 milligram of iron.

48. Zinc and Chromium.—These metals are best determined by evaporating a large quantity of the water to a small bulk, and applying the usual gravimetric methods. The quantitative estimation should be preceded by a qualitative examination of a concentrated sample, and the exact method of procedure made to depend on what is thus learned. In any case, acidulate a large quantity of the water with hydrochloric acid, evaporate to dryness, and heat in an air bath at 120° to 130° until the odor of hydrochloric acid is no longer perceptible. Moisten the residue thoroughly with concentrate hydrochloric acid, and add an appropriate quantity of water, the amount depending on the size of the residue. Heat this solution to boiling, filter off the silica, and wash it thoroughly with hot water. If first or second group metals are present, they must be precipitated by hydrogen sulphide, and the filtrate must be boiled to expel the last trace of this reagent. If the qualitative test has indicated that only chromium and zinc are now present, heat the water to boiling, and slowly add a slight excess of dilute ammonia while stirring continuously. Filter off the precipitated chromium hydrate, and proceed with the determination of chromium as directed in *Quantitative Analysis*, Part 1.

Concentrate the filtrate from the chromium hydrate to a convenient volume, render it distinctly alkaline with sodium carbonate, and then add sufficient acetic acid to render it slightly but distinctly acid, and dissolve any precipitate formed by the carbonate. Heat the solution to incipient boiling, and precipitate the zinc as sulphide by leading a rather rapid current of hydrogen sulphide through the

solution. The zinc may be weighed as sulphide, or the precipitate may be dissolved, and the zinc determined in the solution by one of the methods given in the foregoing Sections.

49. Arsenic.—Arsenic occurs in some waters, and, when present, it should not be overlooked. A qualitative determination is all that is ordinarily required, and for this purpose the Marsh test is generally employed. The details of this process are given in *Qualitative Analysis*, Part 4. When pure zinc is employed in making this determination, the action is very slow at first, and the process becomes quite tedious. Zinc, alloyed with platinum for this purpose, is now on the market, and it appears to be a decided improvement.

If a quantitative determination is required, a large quantity of the water should be evaporated to the proper volume, and the arsenic determined in this by one of the methods previously given.

HARDNESS

50. The determination of hardness has more to do with the scale-forming constituents of a water than with those that have an influence on its character as a drinking water, and, consequently, is probably of greater value in the examination of water for a boiler supply than in the analysis of potable waters. But if the water is for domestic use, a knowledge of how it will act in cooking utensils is of value, and this determination is of considerable importance in examining a water that is to be used for laundry purposes. It is a well known fact that when soap is added to a water containing salts of calcium or magnesium, a considerable portion of the soap is used up in precipitating these metals before any of it is available for detergent purposes. Waters containing these salts are spoken of as hard waters. They are not adapted for laundry use on account of the increased amount of soap required, and the precipitate formed in the water is

undesirable. As we have seen, hardness is divided into permanent and temporary hardness. Temporary hardness is due to salts that are precipitated by boiling the water, and permanent hardness is due to those that remain in solution after the water is boiled. As a rule, the total hardness is all that is required.

Dr. Clark devised a method for the estimation of the hardness of a water by means of a standard soap solution. The soap solution is added to the water until a permanent lather forms, and the hardness is thus learned. This method is in some respects unscientific, but it is nevertheless valuable in many instances. The results were formerly stated in degrees of hardness, and this would be the best method of reporting results if so much confusion had not entered through the use of different quantities of sample; but as degrees based on different quantities are used, such a report is without meaning, unless accompanied by an explanation. To avoid confusion, we prefer to state results in parts per million of calcium carbonate or its equivalent.

51. Standardizing the Soap Solution.—Scrape 10 grams of shavings from a new cake of pure Castile soap, dissolve them in 1 liter of dilute alcohol (2 parts of absolute alcohol to 1 part of water), filter off insoluble matter, if any is present, and keep the solution in a glass-stoppered bottle. To ascertain the strength of this solution, weigh out exactly 1 gram of pure calcium carbonate, and dissolve it in the least necessary quantity of dilute hydrochloric acid. Cautiously add dilute ammonia in sufficient quantity to just neutralize the excess of acid, and dilute the solution to 1 liter. Each cubic centimeter of this solution will contain a quantity of calcium salt equivalent to 1 milligram of calcium carbonate.

Measure 10 cubic centimeters of this standard calcium solution into a glass-stoppered bottle having a capacity of about 250 cubic centimeters, and add 90 cubic centimeters of distilled water. Then add soap solution, .5 cubic centimeter at a time, and shake after each addition, until a lather

is formed that persists for 5 minutes. Note the quantity of soap solution used, and then repeat the experiment, adding .5 cubic centimeter of solution at a time at first, but only .1 or .2 at a time towards the end of the reaction. The exact amount required is thus learned. Now cleanse the bottle, introduce 100 cubic centimeters of pure distilled water, and titrate this with the soap solution in the same way, to learn the amount of soap solution used up by 100 cubic centimeters of pure water. Subtract this amount from the amount used in titrating the standard, to learn the amount used in precipitating the calcium. From this, calculate the value of 1 cubic centimeter of the soap solution in terms of calcium carbonate, and record the factor thus found on the bottle, together with the date of standardization.

An example may render this more clear. Let us suppose that 10 cubic centimeters of the soap solution are used up by the standard, consisting of 10 cubic centimeters of calcium solution and 90 cubic centimeters of distilled water, and that .8 cubic centimeter is used up by 100 cubic centimeters of distilled water. Then, 9.2 cubic centimeters of the soap solution are required for 10 milligrams of calcium carbonate, and the value of 1 cubic centimeter of soap solution in milligrams of calcium carbonate is 1.087. The soap solution should be restandardized at frequent intervals, for it is not permanent, and deteriorates quite rapidly, especially in cold weather.

52. Determination of Hardness.—Measure 100 cubic centimeters of the water into a glass-stoppered bottle of about 250 cubic centimeters capacity, and add soap solution, .5 cubic centimeter at a time, shaking after each addition, until a lather that persists for 5 minutes is formed. When a permanent lather appears to be formed, place the bottle on its side, and allow it to remain in this position for 5 minutes, or until the lather disappears. If the lather disappears in less than 5 minutes, add a little more soap, shake, and again place the bottle on its side. When the lather persists for

5 minutes, the reaction is complete. Now, from the amount of soap solution used, deduct the amount required to produce a permanent lather with 100 cubic centimeters of distilled water, multiply this quantity by the value of 1 cubic centimeter of the soap solution, and multiply the result thus obtained by 10. The total hardness of the water, expressed in parts of calcium carbonate or its equivalent per million, is thus obtained.

In order to obtain the most concordant results, the soap solution should be standardized, and all determinations made at the same temperature, preferably at 15°. It should be remembered that the method is not strictly accurate at best, and, to obtain concordant results, the same method of procedure should be adopted in every case. This is important in adding the soap solution. Not more than .5 cubic centimeter of this should be added at a time, even though the approximate amount required is known. If a water is so hard that 100 cubic centimeters of it require more than 20 cubic centimeters of the soap solution, a second determination should be made, using 50 cubic centimeters of the sample and 50 cubic centimeters of distilled water. Better results are obtained in this way, for the large precipitate formed in the undiluted sample appears to interfere with proper lathering.

It is usually sufficient to determine the total hardness, but, in some cases, the temporary and the permanent hardness are required. When this is the case, determine the total hardness; then boil 100 cubic centimeters of the water, filter off any precipitate formed, add distilled water to make up for the portion evaporated, and determine the permanent hardness in this sample. The difference between the total hardness and the permanent hardness is the temporary hardness.

INTERPRETATION OF RESULTS

53. In no branch of chemical work is the exercise of judgment more necessary than in forming an opinion as to the quality of potable water from the results obtained by

analysis. The chemist should make himself as familiar as possible with the history of the water, and then should consider all the results together in the light of all that is known of the water, and in regard to their bearing on each other. In the case of very good or very bad waters, it is a comparatively easy matter to decide as to their quality; but, with many samples lying between these two extremes, the most careful study is required. The following figures, taken from the standards of purity of drinking water specified by the Michigan State Laboratory of Hygiene, may be of value to the student:

1. The total solids should not exceed 500 parts per million.
2. The chlorine should not exceed 12.1 parts per million.
3. The free ammonia should not exceed .05 part per million.
4. The albuminoid ammonia should not exceed .15 part per million.
5. The oxygen consumed by organic matter should not exceed 2.2 parts per million.
6. The nitrogen as nitrate should not exceed .9 part per million.
7. The best water contains no nitrous acid, and any water that contains nitrites in quantity sufficient to be estimated should not be regarded as a safe drinking water.

These dogmatic statements should not be accepted as final, and indeed no fixed limits can be prescribed, but, as we have pointed out, the results must be considered in their relation to one another, and in the light of what is known of the water. For example, a water contaminated by sewage, and found to contain 12.1 parts per million of chlorine, and .15 part per million of albuminoid ammonia, should be condemned absolutely; while the water of a pond or stream in a heavily wooded district containing salt deposits, might contain these quantities of the constituents mentioned, and still be fairly wholesome.

EXAMINATION OF ICE

54. Chemists are frequently called on to examine samples of ice. In such cases, the ice is allowed to melt, and the water thus obtained is examined in the usual manner. It should not be allowed to melt exposed to the air, however, but should be enclosed in a jar with a tight-fitting glass stopper. A 2-gallon jar with a wide mouth serves well for the purpose. Wash the jar well with distilled water, and introduce the ice in as large pieces as possible, taking care not to touch the ice with the hands more than is necessary. Small fire-tongs, thoroughly cleaned, serve well in handling the ice. Insert the stopper, and allow about one-fifth of the ice to melt at the temperature of the room. Pour off the water, thus thoroughly washing the remaining ice, insert the stopper again, and allow the rest of the ice to melt. Using the water thus obtained as a sample, make the ordinary determinations in the usual manner.

Free ammonia may be present in ice* in about the same quantity as in the water from which it is obtained, but, for the other constituents, the limits of purity are lower.

WATER FOR BOILER SUPPLY

55. Little is cared about the sanitary quality of a water to be used as a boiler supply, but the mineral or scale-forming constituents of the water are important in this case. The principal scale-forming constituents are the carbonates of calcium and magnesium, and calcium sulphate; but, in order to learn the quantities of these constituents present, it is necessary to determine other constituents not generally considered as scale-forming. Sometimes the determination of two or three constituents is all that is required, but such an examination would prove of little service in many cases. A method that will give the most complete idea of the water

* Artificial ice made by the ammonia process frequently contains large amounts of free ammonia due to leaks in the apparatus; such ice may still be perfectly wholesome.

obtainable by the ordinary methods of analysis, is as follows: First determine the total solids as previously directed, as this will serve as a guide in later work, and then proceed with the analysis of the mineral residue. While carrying on this analysis, determine the chlorine and the hardness as previously directed.

56. Determination of Silica.—Measure out an appropriate quantity of the water (from 1 to 10 liters, depending on the amount of solids found), acidify it with hydrochloric acid, and evaporate to dryness in a platinum dish. The evaporation may be carried on over a Bunsen burner, adding successive portions of the water until the sample is all in the dish, and reduced to rather small bulk, but should be completed over a water bath. When dry, remove the dish from the water bath to an air bath, and heat it at 120° to 130° until the odor of hydrochloric acid is no longer perceptible. Moisten the residue thoroughly with concentrate hydrochloric acid, add from 25 to 50 cubic centimeters of water, and boil to dissolve the soluble salts. Filter, wash thoroughly with hot water, ignite in a platinum crucible, and weigh.

If the residue is very small, it is almost certain to be composed entirely of silica, and an examination is scarcely necessary; but if it is of any considerable size, it may contain calcium sulphate, and should be treated as follows: Fuse the residue with sodium carbonate, dissolve the fusion in water and hydrochloric acid, evaporate to dryness, and heat at 120° to 130° to render the silica insoluble. Moisten the residue with hydrochloric acid, add 25 to 50 cubic centimeters of water, and boil to dissolve soluble salts. Filter off the insoluble residue, wash thoroughly with hot water, ignite, and weigh as silica SiO_2 .

Heat the filtrate from the silica to boiling, add ammonia to render it alkaline, and then ammonium oxalate to precipitate the calcium; allow it to stand for at least 3 hours, filter, wash, ignite, and weigh as calcium oxide. Calculate this to calcium sulphate, for this portion of the calcium, at least, occurs as sulphate in the water.

57. Determination of Iron Oxide and Alumina.

Heat the filtrate from the first insoluble residue to boiling, and cautiously add a very slight excess of ammonia. If a copious light-colored precipitate separates, it may contain calcium. In this case, add a little more ammonia, and then dissolve the precipitate in a slight excess of hydrochloric acid. Enough ammonium chloride will thus be formed in the solution to prevent the precipitation of calcium. Now render the solution faintly alkaline with ammonia, continue the boiling for a few moments, allow the precipitate to settle, and filter off the hydrates of iron and aluminum. Wash the precipitate with hot water, ignite in a platinum crucible, and weigh as the oxides of iron and aluminum $Fe_2O_3 + Al_2O_3$. It is unnecessary to separate the oxides in this case, and they should be reported as they are weighed.

58. Determination of Calcium.—At this point, the filtrate will usually be rather large, and should be evaporated to a suitable volume. Then, to the gently boiling liquid, add a few cubic centimeters of ammonia and a moderate excess of ammonium oxalate, continue to boil for a few minutes, and allow the precipitate to settle. Filter, wash thoroughly with hot water containing a few drops of ammonia, ignite intensely over the blast lamp, and weigh as calcium oxide.

59. Determination of Magnesium.—Evaporate the filtrate from the calcium oxalate to a rather small bulk, add a moderate excess of sodium-ammonium phosphate solution while stirring vigorously, add about one-fourth the volume of the liquid of strong ammonia, and cool the solution by standing it in ice water. If a precipitate begins to form at once, when the microcosmic salt or the ammonia is added, the reagent should be introduced, a drop at a time, and the solution stirred after the addition of each drop. Allow the solution to stand 6 hours in a cool place for the precipitate to settle. Filter, wash with one-third-strength ammonia, ignite intensely, and weigh as magnesium pyrophosphate $Mg_2P_2O_7$. Calculate the magnesium to oxide MgO .

60. Determination of Sulphuric Acid.—Acidulate from 1 to 5 liters of the water with hydrochloric acid, evaporate to a small bulk over a burner, and then to dryness on a water bath. Moisten the residue with hydrochloric acid, dissolve it in water, filter off any silica that remains, and wash it thoroughly with hot water. The filtrate should amount to about 100 cubic centimeters. Heat it to boiling, add a moderate excess of barium chloride, and continue the boiling for a few moments. Allow the precipitate to settle, filter, wash with hot water, ignite moderately, and weigh as barium sulphate. From this, calculate the amount of sulphur trioxide in a liter. If a filter paper is used in filtering, the precipitate should be dried and removed from the paper before ignition, to avoid reduction of the precipitate by the burning paper, and a good quality of paper must be used to avoid danger of the precipitate running through. A Gooch crucible is preferred for this purpose by many chemists.

61. Determination of Alkalies.—Acidulate from 1 to 5 liters of the water with a few drops of hydrochloric acid, and evaporate to about 75 cubic centimeters; then add a saturated solution of barium hydrate as long as it produces a precipitate. Heat to boiling, filter, and wash the precipitate until a test of the washings, acidified with nitric acid, fails to give a reaction for hydrochloric acid on the addition of silver nitrate. Evaporate the filtrate to about 75 cubic centimeters, remove from the burner, add a few drops of ammonia, then a strong solution of pure ammonium carbonate as long as a precipitate forms, and allow the solution to stand for some time, stirring occasionally until the precipitate becomes granular. Filter and wash the precipitate with water containing a very little ammonium carbonate and a few drops of ammonia. After adding a few drops of hydrochloric acid, evaporate the filtrate and washings to dryness in a platinum dish over a water bath, place the dish in an air bath heated to about 100°, and gradually increase the temperature to 130° or 140°. Then cautiously heat the

dish to dull redness over a burner to expel ammonium salts, but take care not to heat it sufficiently to volatilize potassium chloride. Dissolve the residue in about 10 cubic centimeters of water, by the aid of very gentle heat, add a few drops of barium hydrate, then a few drops of ammonia, and a slight excess of ammonium carbonate, and allow the solution to stand a short time, stirring occasionally. Filter and wash the precipitate with water containing a very little ammonium carbonate and a drop or two of ammonia. After adding a few drops of hydrochloric acid, evaporate the filtrate to dryness in a weighed platinum dish over a water bath; place the dish in an air bath heated to about 100° , and increase the temperature to about 140° ; then heat it very cautiously over a burner to expel all ammonium salts, cool in a desiccator, and weigh as soon as cool. The residue in the dish now consists of the chlorides of sodium and potassium.

Dissolve the residue of mixed chlorides in the least necessary quantity of water, add a solution of platinum chloride that is as nearly neutral as possible, in excess of the quantity required to unite with all the potassium and sodium present, and evaporate to a pasty consistency on a water bath in which the water is maintained at just about the boiling point, but is not allowed to boil vigorously. Allow the mass to cool, add 35 cubic centimeters of 80-per-cent. alcohol and let it stand in a moderately warm place for an hour, stirring from time to time. If the precipitate is rather large, filter on a paper that has been dried at 120° or in a Gooch crucible, wash thoroughly, but not excessively, with 80-per-cent. alcohol, dry at 120° , and weigh as potassium-platinum chloride K_2PtCl_6 . If the precipitate is very small, it is best, after filtering and washing, to dissolve it with a little water; allow the solution to run into a weighed platinum dish, evaporate to dryness on a water bath, heat at 125° in an air bath, cool, and weigh as K_2PtCl_6 . Calculate the potassium to chloride, subtract this from the weight of mixed chlorides previously obtained, to get the weight of sodium chloride, and calculate the potassium and sodium to oxides K_2O and Na_2O .

6. Grouping the Constituents.—The most rational method of reporting the results of a mineral analysis of a water would be to report just what is found, without attempting to show how the constituents were combined in the water. This method, however, would only show what scale-forming constituents are present to a person acquainted with chemical combination; and to make the analysis as useful as possible, an attempt is usually made to report the compounds as they exist in the water. Careful experiments have shown that if the constituents are grouped according to the following rule, the report will show what compounds exist in waters ordinarily used as potable water or for boiler supply.

Combine the chlorine with the sodium, and if there is more than is required to saturate this, combine it next with potassium; if there is chlorine still left, combine it next with magnesium, and, finally, with calcium. Combine the sulphuric acid with potassium first, if there is any left, and the sodium is not saturated with chlorine; combine the remaining sulphuric acid with the remaining sodium, then with calcium, and, finally, with magnesium. Any of these metals now remaining uncombined are calculated to carbonates. This method of grouping the constituents very nearly represents the facts so far as they can be ascertained for most waters used in boilers and for domestic purposes. There are exceptions to this rule, however, notably in the case of artesian wells, and, especially, mineral waters.

DETERMINATION OF METALS IN ORES

COPPER

63. For the determination of **copper** in ores the methods already given may be used; but as a rapid method of determining copper alone is frequently wanted, a different method of procedure is followed. Three methods are in general use for this determination.

1. *The Electrolytic Method.*—Weigh out an amount of the finely ground ore that will contain from .2 to .4 gram copper, transfer to a casserole, moisten with water, add 25 cubic centimeters of strong nitric acid and 1 cubic centimeter of strong sulphuric acid, cover with a watch glass, and heat until dense choking fumes of SO_3 come off. Cool, moisten with 7 cubic centimeters of dilute (1:1) nitric acid, add 4 drops of strong sulphuric acid and 40 cubic centimeters of water, heat until soluble salts are all in solution. Filter off the insoluble matter and precipitate the copper from the filtrate by electrolysis, as previously described. This method is very extensively used where large numbers of determinations are required. It has the advantage that one man can attend to a large number of analyses; the electrolysis can run at night. On the other hand, it has the disadvantage of requiring expensive apparatus; a single determination cannot be completed as rapidly as by other methods; and care must be exercised to prevent other metals being deposited with the copper.

2. *The Cyanide Method.*—Treat from .5 to 1 gram of finely powdered ore in a flask of about 250 cubic centimeters capacity with 10 cubic centimeters of strong nitric acid, boil down to about 2 cubic centimeters, add 10 cubic centimeters of strong hydrochloric acid, and boil for 3 minutes. Then add 10 cubic centimeters of strong sulphuric acid and boil

until all the hydrochloric and nitric acids are driven off and dense white fumes of SO_3 come off. Allow to cool, and add 10 cubic centimeters of water and about 7 grams of commercial sheet zinc; shake to break up any cake of sulphates. Allow to stand until all the copper is precipitated; 5 minutes is generally long enough. Then add 40 cubic centimeters of water and 20 cubic centimeters of strong sulphuric acid to dissolve the excess of zinc. This is usually complete in 5 minutes. When the zinc has all dissolved, fill the flask with water (tap water may be used) and allow the copper to settle to the bottom; carefully pour off the water, leaving the copper in the flask; fill the flask again with water, allow to settle, and decant the clear liquid. Repeat this washing twice. Finally pour off the water as completely as possible. Add 5 cubic centimeters of nitric acid, boil to expel red fumes, add 1 or 2 drops of hydrochloric acid and 20 cubic centimeters of water. Filter and determine the copper in the filtrate by titration with standard potassium-cyanide solution, as previously described.

3. *The Iodide Method.*—Treat from .5 to 1 gram of the finely powdered ore in a flask of about 250 cubic centimeters capacity with 10 cubic centimeters of strong nitric acid, boil down to about 2 cubic centimeters, add 10 cubic centimeters of strong hydrochloric acid and boil for 3 minutes. Then add 10 cubic centimeters of strong sulphuric acid and boil until all the nitric and hydrochloric acids are expelled and dense fumes of SO_3 are evolved. When cool, add about 35 cubic centimeters of water, and boil. Filter through a small paper, catching the filtrate in a small beaker; wash the flask and insoluble residue with water, keeping the total volume of liquid down to about 75 cubic centimeters. Place in the beaker a piece of sheet aluminum about 2 inches square with the corners bent up at right angles about .5 inch, cover the beaker and boil until all the copper is precipitated. This will take about 10 minutes for 75 cubic centimeters of the liquid; a longer time is required when the liquid is more dilute. Pour the liquid into the flask and wash as much of the copper in with the liquid as possible. A very small

amount will stick to the aluminum. Fill the flask with water, allow the copper to settle, and decant the liquid through a small filter. Fill again with water and continue washing by decantation, pouring all the washings through the small paper until the copper is washed clean. Place the small beaker with the aluminum in it under the funnel and pour 4 cubic centimeters of strong nitric acid, drop by drop, on the paper. This will dissolve the small particles of copper that may have been carried over with the wash water, and, falling in the beaker, will dissolve the copper sticking to the aluminum. Wash with a few cubic centimeters of water. Make sure that all the copper in the beaker is dissolved, and transfer the acid to the flask containing the copper; use as little water as possible to rinse the beaker and aluminum. The same sheet of aluminum may be used for a number of determinations. Boil the liquid in the flask until red fumes cease to come off. Add .5 gram of $KClO_3$ and continue boiling until the volume of liquid is reduced to about 2 cubic centimeters, but do not heat enough to form insoluble basic salts. Add 5 cubic centimeters of water and 5 cubic centimeters of strong ammonia. Make sure that the copper is all in solution. Heat to boiling, and boil 1 minute. Add 6 cubic centimeters of strong acetic acid and 40 cubic centimeters of cold water. Make sure that the copper is all in solution and the liquid acid. Titrate with sodium thiosulphate, as previously described. Where a variety of ores are analyzed, some prefer the volumetric methods to the electrolytic. The cyanide method yields fairly good results and has the advantage of being very rapid. The iodide method yields very accurate results, and, while not so rapid as the cyanide method, is more rapid than the electrolytic.

ZINC

64. Zinc is practically always determined volumetrically by titration with potassium ferrocyanide. A qualitative analysis should always be made, as when cadmium and copper are present the treatment is somewhat different from

that when these metals are absent. In addition to the solutions mentioned under the Ferrocyanide Method for Zinc, two other solutions are needed for their determination.

1. *Potassium-Chlorate and Nitric-Acid Mixture*.—Make a cold saturated solution of $KClO_3$ in concentrate HNO_3 . Put in a flask with several grams of $KClO_3$ to keep it saturated, and keep in a dark place covered with a small inverted beaker. It is not safe to keep this liquid in a tightly stoppered bottle.

2. *Washing Solution*.—Dissolve 10 grams of ammonium chloride in 1 liter of distilled water and add 10 cubic centimeters of strong ammonia.

65. Treatment of Ore.—Weigh 1 gram of the finely pulverized ore into a casserole, cover with a watch glass, add 12 cubic centimeters of concentrate HCl and 3 cubic centimeters of concentrate HNO_3 . When the violent action ceases, evaporate over a flame (leaving the casserole covered) to about 3 cubic centimeters. Cool, add 25 cubic centimeters of the potassium-chlorate and nitric-acid mixture. Add this slowly, and when the violent action has ceased, heat over a free flame, leaving the casserole covered and keeping it in constant motion until the liquid has all evaporated. This requires great care, as there is danger of loss from spattering and it is necessary that all the acid be driven off, but the solid residue must not be overheated. Cool, add 7 grams of ammonium chloride, 15 cubic centimeters of strong ammonia, and 25 cubic centimeters of hot water. Boil for 1 minute and break up any clots with a glass rod. Filter through a large paper and wash with boiling washing solution. If a large precipitate is formed here, it is almost sure to carry part of the zinc. To remove this, transfer the precipitate back to the casserole, evaporate the water, and treat again with the potassium-chlorate and nitric-acid mixture. This is evaporated and treated as before and the two filtrates united. If the ore contains no copper or cadmium, the solution is treated as described under the Ferrocyanide Method for Zinc. If the ore contains copper, after just

neutralizing the ammoniacal solution with hydrochloric acid, add 30 grams of test lead and boil until all the copper is precipitated, or evaporate to a small bulk and precipitate the copper by boiling with aluminum. If cadmium is present, it may be removed with the copper by passing hydrogen sulphide through the slightly acid solution. In case hydrogen sulphide is used, it is not necessary to boil it from the filtrate from the cadmium and copper sulphides before proceeding with the determination.

LEAD

66. Lead may be determined both by gravimetric and volumetric methods. The gravimetric method is the more accurate; but it requires more time and more careful manipulation.

1. *Gravimetric Method.*—Treat 1 gram of the finely pulverized ore in a casserole with 15 cubic centimeters of strong nitric acid. Heat until the ore is decomposed and sulphur oxidized. Then add 10 cubic centimeters of dilute (1:1) sulphuric acid and boil until the nitric acid is driven off and fumes of SO_3 are evolved. Cool, dilute cautiously with about 50 cubic centimeters of water, break up any clots that have formed, and heat in order to dissolve any basic sulphate of iron that may have formed. Allow to cool, filter, and wash the residue with water containing about 1 per cent. of sulphuric acid, then with about 40 cubic centimeters of alcohol. Dissolve the lead sulphate with a hot solution of ammonium acetate made by acidifying strong ammonia with acetic acid. All the lead sulphate can generally be dissolved by three washings with the ammonium acetate. The lead in the ammonium-acetate solution is determined as sulphate, following the directions given under Soft Solder or Pewter.

2. *Volumetric Method.*—Treat from .5 to 1 gram of finely pulverized ore in a casserole with 15 cubic centimeters of concentrate nitric acid and 10 cubic centimeters of concentrate sulphuric acid. When ore is decomposed, carefully heat until all nitric acid is driven off and dense fumes of SO_3

appear. Allow to cool, dilute with cold water, and boil until all soluble sulphates are in solution. Filter, leaving as much of the precipitate in the casserole as possible, wash twice with hot 1-per-cent. sulphuric acid and once with cold water. Wash any precipitate on the paper back into the casserole, using a very small amount of water. Add 30 cubic centimeters of a saturated solution of ammonium carbonate, heat quickly to boiling, and boil for 1 minute in order to decompose any calcium sulphate that may have formed along with the lead sulphate—otherwise the calcium will react on the lead and cause low results. Filter, and wash the precipitate with hot water. Dissolve the washed lead carbonate in concentrate acetic acid, dilute to 180 cubic centimeters, heat to 80° C., and titrate with standard ferrocyanide.

A solution of ferrocyanide for this determination is made by dissolving about 14 grams of pure potassium ferrocyanide in 1 liter of distilled water. One cubic centimeter of this solution corresponds to about .01 gram of lead; but it must be standardized by dissolving weighed amounts (from .2 to .3 gram) of pure lead sulphate in hot ammonium acetate, diluting to 180 cubic centimeters, heating to 80° C., and titrating with the ferrocyanide, using uranium acetate as an indicator, in the same way as the titration for zinc is carried out.

QUANTITATIVE ANALYSIS

(PART 7)

Serial 201G

Edition 2

GAS ANALYSIS

GENERAL PRINCIPLES

1. Although the principles underlying the various forms of gas analysis are themselves of a simple nature, the apparatus employed and the manipulative details involved are in some cases of a comparatively complicated and intricate nature. This is especially the case when the analysis is to be executed with that high degree of exactness essential to scientific research, and, until quite recently, these very exact but also very slow methods of gas analysis were also the only available ones for practical purposes. The growing demand of late years for simpler and more rapid methods, sufficiently accurate for technical purposes, has originated simpler and more rapid methods, and has led to the invention of various forms of gas apparatus, which not only yield good results, but also demand only a minimum amount of time, energy, and operative skill.

It is not within the scope of this Course to dwell upon the more complicated and delicate methods of gas analysis used in research work, but it is our aim to make the student familiar with the simpler and practical determinations he is most likely to be called on to perform.

2. Determination of Gases.—The methods by which gases are determined may be classified according to the following: (1) Absorption of the gas in a suitable reagent and subsequent titration; (2) absorption of the gas in a suitable reagent and subsequent measurement of the residual gas; (3) combustion of the gas, with the subsequent measurement of the contraction and estimation of the carbon dioxide, if any is formed.

A few examples will serve to give the student a general idea of the principles of each of the above enumerated methods.

1. *By Absorption in a Suitable Reagent and Subsequent Titration.*—The carbon dioxide present in a gaseous mixture, as, for instance, air, may be determined by bringing a known volume of the gas into contact with an excess of a standard solution of barium hydrate. Barium carbonate is thereby precipitated, and the excess of barium hydrate is determined by titration with a standard solution of oxalic acid.

2. *By Absorbing the Gas in a Suitable Reagent and Subsequent Measurement of the Residual Gas.*—The carbon dioxide in a mixture of gases is determined by exposing a measured volume of the mixture to the action of potassium hydrate, and, after the whole of the carbon dioxide has been absorbed, the volume of the residual gas is measured. The difference, or the *contraction*, represents the carbon dioxide that was present.

3. *By Combustion of the Gas, with the Subsequent Measurement of the Contraction and Estimation of the Carbon Dioxide, if any is Formed.*—Hydrogen in a gaseous mixture may be estimated by adding to a known volume of the mixture a measured volume of oxygen or air more than sufficient to combine with all the hydrogen. These are caused to unite (by methods to be described later), and the contraction ascertained by again measuring the gas. Since 2 volumes of hydrogen and 1 volume of oxygen unite to form water (which practically occupies no volume), two-thirds of the contraction represents the hydrogen originally present. When the gas to be estimated contains carbon and hydrogen (as in

marsh gas, ethylene, etc.), after the contraction due to combustion has been measured, the volume of carbon dioxide produced is determined by absorption with potassium hydrate and measurement of the residue.

ESTIMATION OF GASES BY ABSORPTION AND SUBSEQUENT TITRATION

ESTIMATION OF CARBON DIOXIDE IN AIR

3. The most varied experience has shown that, through the process of breathing, the air acquires properties that cause it to act deleteriously on health when the products of breathing exceed a certain limit. Since we are not able, by ordinary means, to determine the other substances that are here formed, we make use of von Pettenkofer's suggestion and judge of the purity of the air by the percentage of carbon dioxide present. According to von Pettenkofer, the carbon dioxide in the air should not be raised, by breathing, to over .1 per cent.

The process best suited to the quantitative determination is that first used by Saussure and modified by von Pettenkofer, and generally known as **von Pettenkofer's methods**. The sample of air to be examined is contained in a large, wide-mouthed glass jar, the exact capacity of which is known, and that can be closed with an air-tight fitting rubber stopper. The temperature of the air and the atmospheric pressure are noted at the time the sample is taken. A measured volume of a solution of barium hydrate of known strength is introduced into the jar, and thoroughly shaken up with the enclosed air until the carbon dioxide is all absorbed. Aliquot portions of the liquid are then withdrawn, and titrated with a solution of oxalic acid of known strength.

4. Standard Oxalic Acid.—In order to simplify the subsequent calculations, the strength of the oxalic-acid solution

may be made up so that 1 cubic centimeter is equivalent to 1 cubic centimeter carbon dioxide measured under standard conditions, that is to say, 1 cubic centimeter of the acid is capable of saturating a quantity of barium hydrate that would be decomposed by this volume of carbon dioxide, the weight of which is .00197 gram. Oxalic acid of this strength would contain 5.6414 grams of the crystallized acid $H_2C_2O_4 \cdot 2H_2O$ in 1 liter; but, as dilute solutions of oxalic acid are not stable, it is advisable to prepare a solution that contains 56.414 grams of $H_2C_2O_4 \cdot 2H_2O$ per liter, and to withdraw an aliquot proportion and dilute it whenever required. Thus, 56.414 grams of dry, crystallized oxalic acid are exactly weighed out, dissolved in cold, air-free water (that is, distilled water that has been recently boiled to expel all carbon dioxide, and quickly cooled), and the solution made up to 1 liter. For use, 10 cubic centimeters are transferred to a 100-cubic-centimeter flask by means of a pipette, and the solution diluted to 100 cubic centimeters with air-free water.

5. Barium-Hydrate Solution.—Place 40 to 50 grams of crystallized barium hydrate $Ba(OH)_2 \cdot 8H_2O$, powdered or crushed, in a large glass-stoppered bottle, and add 1 liter of water. The mixture is thoroughly shaken from time to time, until the water is saturated, after which it is allowed to settle. The clear liquid is carefully decanted or filtered into another glass-stoppered bottle, and diluted with an equal volume of water. This solution will possess approximately the same relative strength as that of the oxalic acid previously mentioned. A solution of exact equivalent strength, of which 1 cubic centimeter = .00197 gram CO_2 (i. e., 1 cubic centimeter CO_2 at normal temperature and pressure), would contain 14.11 grams of $Ba(OH)_2 \cdot 8H_2O$ per liter. Such a solution cannot be obtained by direct weighing, as, the salt being efflorescent, its state of hydration is uncertain; and it also absorbs atmospheric carbon dioxide. A saturated solution at the ordinary temperature contains about 32 grams per liter; hence, if this be diluted with its

own volume of water, the solution, as first prepared, will contain about 16 grams per liter. As the solution constantly undergoes change by the absorption of atmospheric carbon dioxide, its value must be determined every time before it is used by titration against the standard oxalic acid. The stopper of the bottle containing the barium-hydrate solution should be greased, so as to exclude the air as much as possible.

6. Standardizing the Barium-Hydrate Solution.—

In a small flask are placed 20 cubic centimeters of standard oxalic acid and then 25 cubic centimeters of the barium-hydrate solution added. The solution is then neutralized by slowly running in more oxalic acid by means of a burette until the liquid ceases to give any indication of a brown color when a drop of it is placed on a piece of turmeric paper. The alkali is gradually neutralized by the oxalic acid; the brown color, which at first is very evident, gradually shows more and more as a faint fringe of color round the edge of the moistened spot on the turmeric paper, until finally it disappears. Suppose, for instance, that 28 cubic centimeters of the oxalic acid are used; then, 100 cubic centimeters of this barium-hydrate solution would require 112 cubic centimeters of the oxalic acid to exactly neutralize it.

7. Determination of Carbon Dioxide.—

A large glass jar, whose mouth is sufficiently wide to admit the hand, so that it may be conveniently wiped dry inside with a cloth, is fitted with a rubber stopper. A hole is bored in the stopper, and this hole is closed with a piece of glass rod. The capacity of the jar is ascertained by filling it with water up to the stopper, and measuring the volume of the water. As it is evident that when the amount of carbon dioxide present is small, the accuracy of the determination is increased by using larger volumes of air; it is advisable that the jar should hold from 8 to 10 liters, if possible, but not less than 5 liters. Its exact capacity should be scratched on the vessel.

The jar is filled with the air to be tested by leading into it, right to the bottom of the jar, a piece of rubber tubing attached to a pair of bellows and blowing a stream of air for about 5 to 6 minutes, in order to insure complete displacement of the air already in the vessel. The stopper is then inserted. The temperature of the air in the immediate vicinity of the jar is noted, and also the height of the barometer at the same time. By means of a pipette, 100 cubic



FIG. 1

centimeters of the barium-hydrate solution are then delivered in the jar through the hole in the stopper, and the glass rod is immediately replaced. The liquid is then made to wet the surface of the glass by slowly revolving the vessel upon its side; and it is left in contact with the gas, being shaken at intervals for about 30 to 40 minutes, by which time all the carbon dioxide will have been absorbed. When the absorption of the carbon dioxide is complete, 25 cubic centimeters of the turbid liquid are withdrawn by means of a pipette; to which a piece of glass tubing has been attached in order that the bottom of the jar may be reached. This arrangement is introduced through the hole in the rubber stopper, as shown in Fig. 1. When the pipette is full, the piece of rubber is detached, and the liquid allowed to drip from the pipette until

it reaches the graduation mark. The measured volume is then transferred to a beaker, and immediately titrated with oxalic acid, exposure to the air being avoided as much as possible. The end of the reaction is indicated by means of turmeric paper, used as described in Art. 6. A duplicate titration should be made with a second portion of the liquid. Some chemists prefer to use a solution of phenol phthalein in alcohol as an indicator. In this case, about 2 cubic centimeters of this indicator are added to the liquid, and the

oxalic acid added until the liquid becomes neutral, which is indicated by the disappearance of the color.

Since 25 cubic centimeters (out of the 100 cubic centimeters of the barium-hydrate solution originally placed in the jar) have been used for titration, the volume of oxalic acid used, multiplied by 4, will give the amount of oxalic acid required to neutralize the 100 cubic centimeters of the barium-hydrate solution after the absorption of the carbon dioxide in the known volume of air. This, obviously, will be less than that required by 100 cubic centimeters of the original barium-hydrate solution by just the volume of carbon dioxide that was contained in the sample of the air.

The following details of an analysis will make this determination perfectly understood:

Capacity of glass jar = 10.5 liters

Temperature of the air = 17°

Barometer reading = 769 mm.

$$\text{Then, } \frac{10.5 \times 273 \times 769}{(273 + 17) \times 760} = 10.001 \text{ liters,}$$

which is equal to the volume of the sample at normal temperature and pressure.

The value of the barium-hydrate solution is 100 c. c. = 112 c. c. of the standard oxalic-acid solution; 100 c. c. of the barium hydrate were used for absorption; 25 c. c. were taken out for titration; 25 c. c. required 27.10 c. c. of standard oxalic acid; therefore, 100 c. c. would require $27.10 \times 4 = 108.4$ c. c. oxalic acid. $112 - 108.4 = 3.6$ c. c. = the volume of oxalic acid, which is equivalent to the carbon dioxide absorbed by the 100 c. c. of barium-hydrate solution.

But, since 1 c. c. of oxalic acid = 1 c. c. CO_2 at normal temperature and pressure, 3.6 c. c. oxalic acid = 3.6 c. c. CO_2 present in 10.001 liters or 10,001 c. c. of air.

$$\text{Therefore, } \frac{3.6 \times 100}{10,001} = .0359 = \text{percentage of } CO_2, \\ \text{by volume}$$

8. Since the presence of barium carbonate does not interfere with the titration, some chemists prefer to titrate

directly in the same vessel in which the air has been collected. This method has the advantage that the barium-hydrate solution is the least exposed to air. For this purpose, a liter flask is employed, which is fitted with a rubber stopper having two perforations that are closed with pieces of glass rod. After sampling the air and adding 10 cubic centimeters of barium-hydrate solution, the burette containing the standard oxalic acid is inserted into one of the perforations, as shown in Fig. 2, and the titration carried out as previously described. As an indicator, about 1 cubic centimeter of phenol phthalein in alcohol is used. The titration is finished as soon as the last trace of color disappears. If the increased pressure resulting inside the flask checks the flow of the liquid from the burette, this pressure is removed by lifting the glass stopper closing the second perforation. The only disadvantage of this

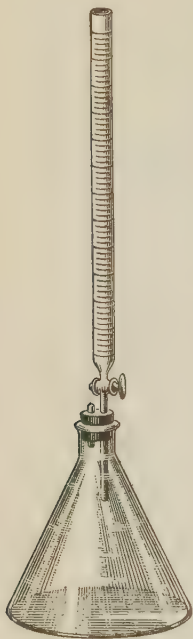


FIG. 2

method is that but a comparatively small volume of air can be used.

ESTIMATION OF SULPHUR DIOXIDE IN FURNACE GASES

9. By means of a pipe inserted into the flue, a measured volume of the furnace gases is aspirated, with a suitable aspirator, through a known volume of a dilute standard solution of iodine, and the excess of iodine titrated with a standard solution of sodium thiosulphate.

10. Standard Iodine Solution.—Pure resublimed iodine to the amount of 12.7 grams, is powdered and weighed out into a liter flask. About 20 grams of potassium iodide (free from iodate), dissolved in 100 cubic centimeters of water, are added, and the mixture gently shaken until the

iodine is entirely dissolved. The solution is then diluted up to the liter with water at 15° and preserved in a well-fitting stoppered bottle in the dark; 1 cubic centimeter of this solution will contain .0127 gram of iodine, and is equivalent to .0032 gram of SO_2 . It is, however, more convenient in this case and simplifies the calculation, to employ solutions of such strength that 1 cubic centimeter shall equal 1 cubic centimeter SO_2 measured at normal temperature and pressure, i. e., .002867 gram SO_2 instead of .0032. Such a solution will contain 11.379 grams of iodine per liter, and may be most conveniently obtained by diluting 100 cubic centimeters of the above solution to 111.6 cubic centimeters. In case the percentage of SO_2 in the gas under examination is comparatively small, it is better to employ a solution of one-tenth this strength, in which 1 cubic centimeter = .1 cubic centimeter SO_2 .

11. Standard Sodium-Thiosulphate Solution.—To obtain a standard solution, 1 cubic centimeter of which is equivalent to 1 cubic centimeter SO_2 , i. e., .002867 gram SO_2 , 22.22 grams of sodium thiosulphate $Na_2S_2O_3 \cdot 5H_2O$, which has been carefully powdered, are weighed out into a liter flask and dissolved in water. The solution is then diluted to the 1,000-cubic-centimeter mark with water at 15° . If 100 cubic centimeters of this solution are again diluted to 1,000 cubic centimeters, each cubic centimeter is equivalent to .1 cubic centimeter SO_2 . As it is practically impossible to obtain sodium thiosulphate containing exactly the theoretical amount of water of crystallization, it is preferable to weigh out about 23 grams of the salt, and titrate it against the iodine solution of known strength, and from the results, calculate the amount of water that has to be added to make 1 cubic centimeter equivalent to exactly 1 cubic centimeter of the iodine solution.

12. Starch Solution.—The starch solution, serving as an indicator, is prepared by mixing 1 or 2 grams of dry starch in a medium-sized beaker with 5 or 6 cubic

centimeters of cold water. A considerable quantity of boiling water is then poured on it. As the hot water is being added, the opaque white appearance, which the mixture presents at first, changes almost suddenly to that of a semi-translucent gelatinous substance. At this point, the addition of the boiling water is stopped, and the beaker nearly filled up with cold water. It is allowed to settle, and the clear liquid poured off for use. This starch solution should be made up fresh every time, as it will not keep more than a day.

13. Determination of Sulphur Dioxide.—The apparatus used in this determination is known as **Reich's apparatus**; it consists of a double-necked absorption bottle *a*, the aspirator *b*, and the glass cylinder *c*. These are supported by a convenient stand, as shown in Fig. 3. The rubber tube joining *a* and *b* is about 30 centimeters long;

100 cubic centimeters of the $\frac{n}{100}$ iodine solution are placed in the bottle *a* and the aspirator *b* is filled with water. Before

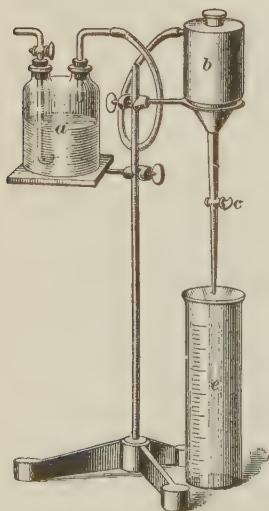


FIG. 3

making a determination, the air in the tubes leading to the apparatus is displaced by the gas to be examined. The apparatus is tight if, after a short time and as soon as the air in *a* is correspondingly expanded, the water ceases entirely to flow from the aspirator. In making the determination, the stop-cock *c* is opened, and sufficient water from the aspirator *b* to draw over 8 to 10 liters of gas through the iodine solution is measured in the cylinder *c*. During the determination, the bottle *a* is frequently shaken. The volume of water that has run out is equal to that of the gas taken, and the quantity of sulphur dioxide

can approximately be told from the amount of iodine used. During the experiment, the temperature of the water is taken (which will be the temperature of the gas) and the height of the barometer is noted.

When 8 or 10 liters* of gas have in this way been aspirated through the iodine solution, the process is stopped, and 25 cubic centimeters of the iodine solution are transferred to a beaker and titrated with the standard sodium thiosulphate. As soon as the red-brown color of the iodine solution changes to a straw color, 1 or 2 drops of dilute starch solution are added, and the titration continued, drop by drop, until the blue color is entirely discharged. A duplicate titration is made in a second portion of the solution.

The following record of an analysis will make this determination more clear.

Gas drawn from the flue of a coke furnace:

Volume of water drawn from aspirator = 8.25 liters

Temperature = 16°

Atmospheric pressure = 765 mm.

Volume of gas operated upon equals

$$\frac{(8.25 \times 273) \times 765}{(273 + 16) \times 760} = 7.8445 \text{ liters}$$

at normal temperature and pressure.

100 c. c. of iodine solution are employed in the absorption flask.

1 c. c. = 1 c. c. of thiosulphate = .1 c. c. SO_2 at normal temperature and pressure.

After absorption, 25 c. c. of iodine solution required 18.2 c. c. sodium thiosulphate.

* When the gas is very rich in sulphur dioxide, as, for instance, in the flue gases from the sulphur burner in vitriol works, a much smaller volume, say 1 liter, need be drawn through the apparatus, and, in the final correction of the volume of gas operated on, the volume of sulphur dioxide that has been absorbed must be added to the volume of water measured out of the aspirator. In the example here given, where the amount of sulphur dioxide is small, these corrections are left out, as they would not affect the third decimal figure.

Volume of thiosulphate required for 100 c. c. = $18.2 \times 4 = 72.8$ c. c., and volume of SO_2 absorbed equals

$$\frac{100 - 72.8}{10} = 2.72 \text{ c. c.}$$

Hence, 7,844.5 c. c. of the furnace gas contain 2.72 c. c. SO_2 ,
or

$$\frac{2.72 \times 100}{7,844.5} = .0346 \text{ percentage } SO_2 \text{ by volume}$$

ESTIMATION BY ABSORPTION AND MEASUREMENT OF RESIDUAL GAS

14. The processes employed by this method differ from the foregoing, in that they involve (1) manipulation of comparatively small volumes of gas, and (2) the accurate measurement of these volumes.

For the manipulation of small volumes of gas, special apparatus is required; and for the accurate measurement of gaseous volumes, special precautions are necessary.

15. Simple Gas Burette.—The simple gas burette, which is shown in Fig. 4, consists of two glass tubes *a* and *b*, which are set in iron feet and are connected by a thin rubber tube about 120 centimeters long. To facilitate the cleaning of the burettes, the rubber tube is cut in two parts, and the two ends joined by a piece of glass tubing. Inside the feet, the tubes *a* and *b* are bent at right angles and conically drawn out. The end projecting from the iron is about 4 millimeters external diameter, and is somewhat corrugated, so that the rubber can be tightly fastened to it by winding it with thin wire. The measuring tube *b* ends at the top in a thick-walled tube *c* of from $\frac{1}{2}$ to 1 millimeter internal diameter, and about 3 centimeters long. Over this, a short piece of new, black, rubber tubing *d* is wired on. The rubber tube is closed by a Mohr pinch cock *f*, which is put on close to the end of the capillary. The graduated measuring tube *b* holds 100 cubic centimeters, the lowest mark being slightly above the iron foot. The cubic centimeters are divided into fifths, and the

graduation runs up and down. The tube *a*, generally known as the level tube, is somewhat widened at the upper end, to facilitate the pouring in of liquids.

16. Manipulation of the Gas Burette.

Fill the tubes *a* and *b*, Fig. 4, with water, taking care to drive all the air out of the connecting rubber tube by either raising or lowering the tubes; then join the burette to the vessel containing the gas by means of a glass or rubber tube filled with water. This connecting tube can be easily filled with water by raising the level tube.

To fill the burette with the gas to be examined, grasp the tube *a* in the left hand, close the rubber tube by pressing it between the little finger and the palm of the hand, and pour out the water in *a*. Place the level tube on the floor and open the pinch cock *f*. The water will now flow into the level tube and the gas will be drawn into the burette. When *b* is filled with the gas, close the pinch cock *f*, disconnect *b* from the gas holder, and, after the liquid has run down

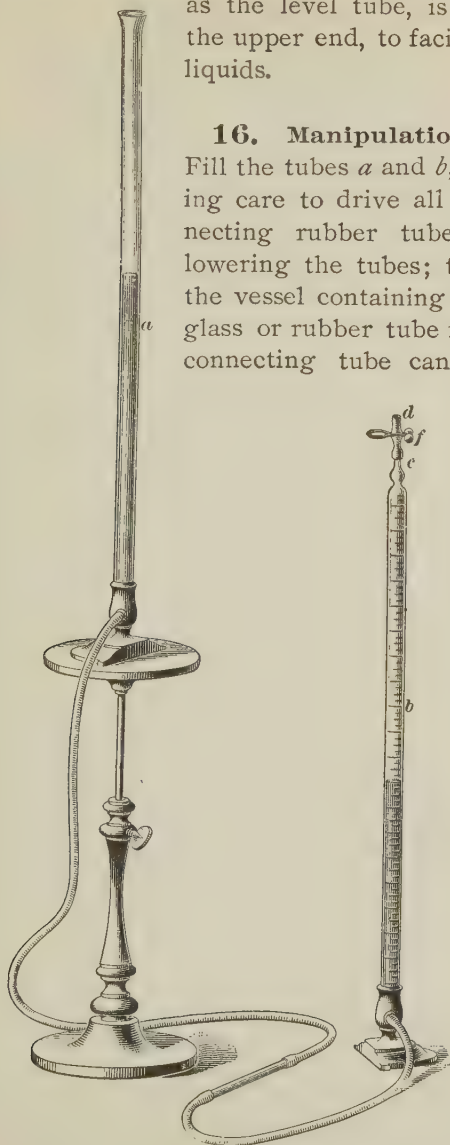


FIG. 4

from the walls of the burette, take up the tubes by the iron

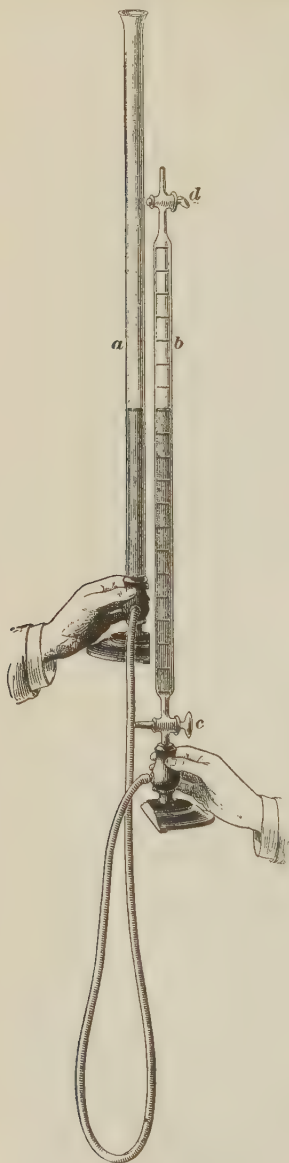


FIG. 5

feet and, by raising or lowering, bring the water in the tubes to the same level. The gas is now under atmospheric pressure and its volume is read off. To measure off exactly 100 cubic centimeters, bring somewhat more than 100 cubic centimeters of the gas into the burette, close the latter with the pinch cock, and allow the water to run down the walls of the burette. Now compress the gas to a little less than 100 cubic centimeters by raising the level tube, close the rubber tube with the thumb and first finger of the left hand, set the level tube on the table, and, raising the burette with the right hand to the level of the eye, carefully open the rubber tube and let the water run back until the meniscus stands at the 100-cubic-centimeter mark. Keeping the rubber still compressed, open the pinch cock for a moment. The excess of the gas will escape, and there remains in the burette exactly 100 cubic centimeters of gas under atmospheric pressure.

17. Modified Winkler Gas Burette.—The modified Winkler gas burette shown in Fig. 5 consists of the level tube *a* and the measuring tube *b* connected by a thin rubber tube about 120 centi-

meters long. The glass tube *b* is about 100 cubic centimeters capacity, provided with the simple glass stop-cock *d*, and the three-way stop-cock *c*, which allows of communication being established with the level tube or with the outer air at will. This will be seen more clearly in Fig. 6. The space between the two stop-cocks is divided into exactly 100 equal parts, with subdivisions of one-fifth cubic centimeter each, and the graduations are numbered in both directions. The thick-walled tube (Fig. 5) must have a diameter of from only $\frac{1}{2}$ to 1 millimeter, so that bubbles of the gases that are passed in and out cannot stop in this tube. The manipulation of the burette is practically the same as that described in the preceding article.

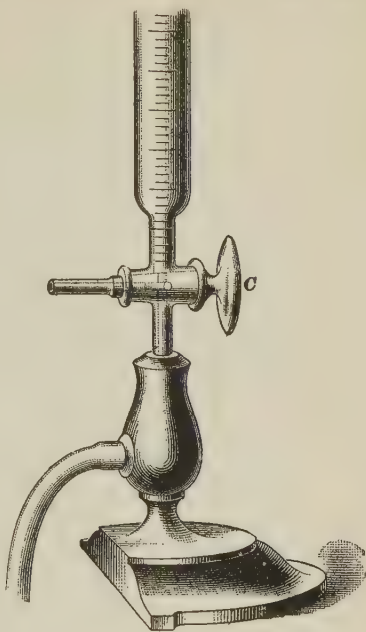


FIG. 6

18. Correction of Gaseous Volume.—The volume of gas has been briefly treated in sections on *Physics* and *Inorganic Chemistry*, but a short repetition and expansion of the subject appears appropriate here. It has been stated in the sections mentioned, that the volume of a given weight of a gas depends on the pressure and the temperature; in gas analysis, however, a third factor has to be taken into account, namely, the degree of humidity of the gas at the time the measurement is made.

In order, therefore, that the various volumes observed during an analysis shall be comparable with one another, it is necessary either that the conditions mentioned should remain constant throughout, or that the volumes measured

under different conditions should be reduced by calculation to one common standard.

In exact methods of analysis, the latter plan is invariably adopted, but in the more rapid and somewhat rougher methods employed for technical purposes, the analysis may usually be carried out without disturbing the uniformity of conditions to an extent that will introduce any material error in the results. The recognized standard to which gaseous volumes are reduced is the volume that the gas would occupy at 0° and under a pressure of 760 millimeters, *when in the dry state*.

19. Correction of Temperature.—The coefficient of expansion is usually taken as $\frac{1}{273}$, or .003665; therefore, the volume at 0° equals the volume at t° divided by $1 + .003665 t$. Hence,

$$V_0 = \frac{V}{1 + .003665 t} \text{ or } \frac{V \times 273}{273 + t} \quad (1)$$

where V_0 = volume at 0° , and V = volume at t° .

20. Correction of Pressure.—According to Mariotte's law, quoted in previous Sections, the volume of a gas being inversely as the pressure,

$$V_0 = \frac{VP}{760} \quad (2)$$

where V = volume at P pressure; or, making the corrections for temperature and pressure together, we obtain the formula

$$V_0 = \frac{VP}{760(1 + .003665 t)} \text{ or } \frac{VP \times 273}{760 \times (273 + t)} \quad (3)$$

21. Correction for Tension of Aqueous Vapor.—The aqueous vapor present in a gas exerts a pressure in opposition to the barometric pressure; hence, the volume of gas is increased by the presence of aqueous vapor. If the gas is saturated with aqueous vapor, and an excess of water, however indefinitely small, is present, then the pressure or tension of the aqueous vapor is independent of change of pressure, varying only with change of temperature. The *tension of aqueous vapor* has been experimentally determined for every degree of temperature, and in Table I will be found the tension or pressure, in millimeters of mercury, of the vapor of water between the temperatures 5° and 30° .

TABLE I

TENSION OF AQUEOUS VAPOR IN MILLIMETERS OF MERCURY FOR EACH FIFTH OF A DEGREE FROM 5° TO 30°

C°.	t mm.	C°.	t mm.	C°.	t mm.	C°.	t mm.	C°.	t mm.
5.0	6.5	10.0	9.2	15.0	12.7	20.0	17.4	25.0	23.5
.2	6.6	.2	9.3	.2	12.9	.2	17.6	.2	23.8
.4	6.7	.4	9.4	.4	13.0	.4	17.8	.4	24.1
.6	6.8	.6	9.5	.6	13.2	.6	18.0	.6	24.4
.8	6.9	.8	9.7	.8	13.4	.8	18.3	.8	24.7
6.0	7.0	11.0	9.8	16.0	13.5	21.0	18.5	26.0	25.0
.2	7.1	.2	9.9	.2	13.7	.2	18.7	.2	25.3
.4	7.2	.4	10.1	.4	13.9	.4	19.0	.4	25.6
.6	7.3	.6	10.2	.6	14.1	.6	19.2	.6	25.9
.8	7.4	.8	10.3	.8	14.2	.8	19.4	.8	26.2
7.0	7.5	12.0	10.5	17.0	14.4	22.0	19.7	27.0	26.5
.2	7.6	.2	10.6	.2	14.6	.2	19.9	.2	26.8
.4	7.7	.4	10.7	.4	14.8	.4	20.1	.4	27.1
.6	7.8	.6	10.9	.6	15.0	.6	20.4	.6	27.4
.8	7.9	.8	11.0	.8	15.2	.8	20.6	.8	27.7
8.0	8.0	13.0	11.2	18.0	15.4	23.0	20.9	28.0	28.1
.2	8.1	.2	11.3	.2	15.6	.2	21.1	.2	28.4
.4	8.2	.4	11.5	.4	15.7	.4	21.4	.4	28.7
.6	8.3	.6	11.6	.6	15.9	.6	21.7	.6	29.1
.8	8.5	.8	11.8	.8	16.1	.8	21.9	.8	29.4
9.0	8.6	14.0	11.9	19.0	16.3	24.0	22.2	29.0	29.7
.2	8.7	.2	12.1	.2	16.6	.2	22.5	.2	30.1
.4	8.8	.4	12.2	.4	16.8	.4	22.7	.4	30.4
.6	8.9	.6	12.4	.6	17.0	.6	23.0	.6	30.8
.8	9.0	.8	12.5	.8	17.2	.8	23.3	.8	31.1
								30.0	31.5

NOTE.—In cases where the tension rises .1 millimeter for a rise of .2°, the same pressure for the intermediate tenth degree may be taken as that given for the temperature immediately preceding it. Thus, for the temperature 10.1°, the tension 9.2 millimeters will be taken. For very accurate work, fuller tables given to the third decimal should be consulted.

In making the necessary correction for aqueous vapor, therefore, the number of millimeters of mercury representing the tension of aqueous vapor at that particular temperature at which the gas is measured, is deducted from the barometric pressure to which the gas is exposed. For

example, a gas is measured at 763 millimeters, and the temperature is 13.4° ; then, by referring to Table I, the tension at 13.4° is seen to be 11.5 millimeters. Deducting this from the barometric pressure, we obtain $763 - 11.5 = 751.5$ millimeters of true pressure.

If p stands for the pressure due to aqueous vapor, then the formula

$$V_0 = \frac{V(P-p)}{760(1 + .003665 t)}, \text{ or } \frac{V(P-p) \times 273}{760 \times (273 + t)} \quad (4)$$

expresses the necessary corrections to reduce a volume of gas, saturated with aqueous vapor, to the standard conditions.

22. When gases are confined over water, as in the gas burettes just described, the conditions of complete saturation with aqueous vapor are, of course, always present, and when mercury is employed as the confining liquid, complete saturation of the gas with aqueous vapor is insured by introducing a drop of water into the measuring tube. With this apparatus also, the gas volumes are always read at the atmospheric pressure, and, as the analytical operations are rapidly performed, changes of barometric pressure sufficient to influence the results need not be anticipated. Changes of temperature, however, must be guarded against as far as possible, and, with this object in view, it should be made an imperative rule never to handle the glass parts of gas analytical apparatus. In order to ascertain the temperature of the gas and see how far it is being maintained uniform throughout, a simple and convenient plan is to suspend a thermometer inside the level tube by means of a thread, so that it reaches nearly to the bottom, and remains there during the whole analysis. As the water is continually being passed backwards and forwards from the level tube to the measuring tube, the temperature of the gas may be taken as the same as that of the water over which it is confined, and, if the temperature of the latter does not materially change, that of the gas may be considered as practically uniform.

23. As previously stated, when conditions under which gas measurements are made are constant, it is not necessary

to reduce the observed volume to the standard conditions. This will be rendered more obvious from the following example:

The original volume of gaseous mixture in the burette measured 100 cubic centimeters at ordinary pressure (i. e., when the water was at the same level in both tubes). One constituent x was then removed by absorption and the gas measured again. Its volume now was 75 cubic centimeters at atmospheric pressure. The temperature was 16° and the barometric pressure 758 millimeters throughout.

Then (1) without making reduction to standard conditions we obtain

$$100 - 75 = 25 = \text{percentage of } x \text{ in the mixture}$$

(2) On reducing the two volumes by means of formula 4,

$$V_0 = \frac{V(P-p)}{760(1 + .003665 t)}$$

we obtain

$$(a) V_0 = \frac{100 \times (758 - 13.5)}{760 \times (1.05864)} = 92.534$$

$$(b) V_0 = \frac{75 \times (758 - 13.5)}{760 \times (1.05864)} = 69.276$$

Therefore, $92.534 - 69.276 = 23.258 =$ volume of x in 92.534 cubic centimeters of original gas, and

$$\frac{23.258 \times 100}{92.534} = 25 = \text{percentage of } x \text{ in the mixture}$$

Since the tension of aqueous vapor is independent of pressure, then, in the event of any alteration of barometric pressure taking place during an analysis, it is only necessary to make a correction for pressure—not necessarily by reducing all the volumes to the standard, but by reducing all to the same pressure as any of them.

Thus, in the above, suppose that between the two measurements the barometer fell from 758 to 752 millimeters, the temperature remaining constant at 16° , then the following are the data:

Original volume = 100 c.c. at 16° and 758 mm.

After absorbing x , volume = 75 c.c. at 16° and 752 mm.

Then, $\frac{75 \times 752}{758} = 74.41 =$ volume that the residual gas would occupy if measured under the same conditions as the original volume.

Hence, $100 - 74.41 = 25.59 =$ percentage of x in the mixture.

If, now, from the above data, the two volumes be reduced to standard conditions by means of formula 4, it will be found that the same result is obtained, namely, 25.59 percentage of x .

Again, since the tension of aqueous vapor depends on the temperature, increasing with the rise of temperature, change of temperature will obviously produce an alteration of the pressure, even though the barometric pressure remains constant. For example, suppose, in the above illustration, the 100 cubic centimeters of original volume are measured at 16° and the 75 cubic centimeters of residual gas are measured at 20°, the barometer standing uniformly at 760 millimeters, then the actual pressure in the first case is $760 - 13.5$ (tension of aqueous vapor at 16°), and in the second it is $760 - 17.4$ (tension at 20°).

Hence, if any change of temperature is observed in the gas during the progress of an analysis, the observed volumes must be reduced to the standard by means of formula 4,

$$V_0 = \frac{V(P-p)}{760(1 + .003665 t)}$$

24. Collection of Gas for Analysis.—If the gas for analysis is collected in the laboratory, as, for instance, a sample of ordinary illuminating gas, it may be introduced into the burette by first placing the measuring tube on a higher level than the level tube, and allowing the former to empty. By means of the three-way cock, shown in Figs. 5 and 6, communication between the measuring tube and the outer air is then opened, and a rapid stream of the gas passed through the tube from the top, until the air has been entirely swept

out. The upper tap is then closed and the lower one turned so as to reestablish communication with the level tube.

When the available supply of gas is comparatively small, it may be collected in a glass tube over water (or, if necessary, over mercury), and afterwards transferred to the burette, as described below. The tube may conveniently have the form shown in Fig. 7. It is first filled with water by sucking the liquid up and closing the rubber tube with a pinch cock, and the gas is then passed up from below in the usual manner. The tube is then connected to the gas burette, with the same precautions against enclosing air in the joints, as given below. When the gas is collected away from the laborator— it should be taken in glass tubes drawn out to a capillary constriction at each end. These tubes are filled either by aspirating the gas through them so as to sweep out the air, and then hermetically sealing them at the constriction, or by taking them to the spot in a vacuum and sealed condition, and then breaking open one end in the gas to be collected. After the gas has filled the tube, the end is again hermetically sealed by means of a blowpipe.

In order to transfer the gas from the sealed tube to the burette, a piece of capillary tube *t*, bent twice in right angles, is attached to the latter, as shown in Fig. 7, the joints

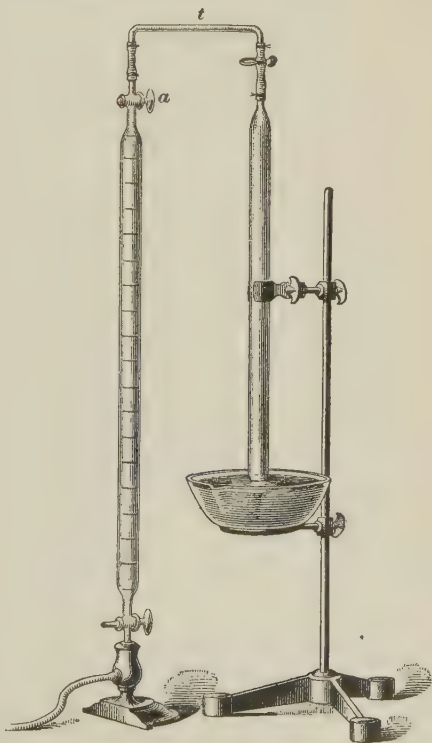


FIG. 7

being wired round. The level tube is then raised, until water completely fills the measuring tube and drops from the open end of the bent capillary. Whenever the available supply of the gas to be analyzed renders such a course possible, the water used in the burette should be first saturated with the gas by shaking a quantity of water with some of the gas in a stoppered bottle for a few minutes. Near each end of the sealed tubes, a slight scratch with a file is made. Over one end, a short piece of rubber tube is slipped, and the projecting portion of it filled up with water. The bent capillary, already entirely filled with water, is then introduced into this tube, and the latter secured with binding wire. In this way, all air is excluded from the joint. The lower end of the tube is dipped into a vessel of water. The tube is broken at the file mark within the rubber joint, and the end beneath the water is also broken off by means of a pair of pliers. On lowering the level tube and opening the

stop-cock *a* at the top of the measuring tube, the gas will be drawn over into the burette.

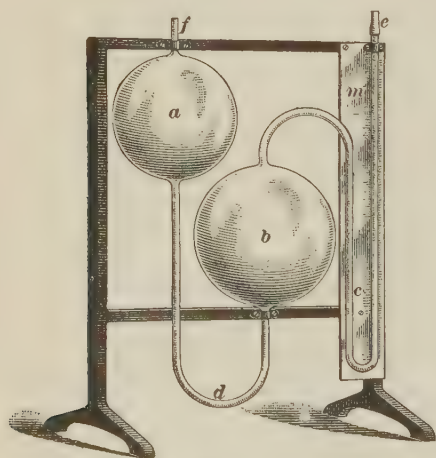


FIG. 8

25. Absorption of Gases.—Except when the absorbing liquid is water, in which case the absorption would be made directly in the measuring tube of the burette, the absorption of the gases in a mixture is carried out in a separate piece of apparatus

known as *absorption pipette*. The *simple absorption pipette* shown in Fig. 8 consists of two glass globes *a* and *b*; the capacity of *b* should be at least 150 cubic centimeters, so that when the gas from the full burette (100 cubic centimeters) is transferred to it, sufficient room remains for

an adequate quantity of the reagent. The two globes are connected by means of a bent glass tube *d*, and are fastened to a wooden stand to prevent breakage. A capillary tube *c* passes from the globe *b* before a plate of milk glass *m*, which is let into the wooden stand, in order to be able to trace readily the movements of the liquid thread in the capillary tube *c*. The exit tube *f* of the globe *a* and capillary tube *c* extend above the wooden frame; a small rubber tube *e* is connected to the protruding tube *c* and fastened by means of wire, and the tube furnished with a pinch cock. The reagent to be used is poured in at *f* (for which purpose a thistle funnel should be used to avoid spilling the reagent over the outside), filling the globe *b* entirely, *a* only partially, and the capillary tube *c* to the junction with the rubber tube near *e*. When not in use, *f* is closed by a cork and *c* by a glass rod, not with the pinch cock, which spoils the rubber tube after a short time. A separate pipette is used for each reagent, and a label designating the contents of the pipette should be attached to the wooden frame of each.

26. Manipulation of Single-Absorption Pipette.

To analyze a gas with the single-absorption pipette, the burette is filled with distilled water that has been previously saturated by shaking with the gas in question. The pipette is so filled with the absorbent that the bulb *a*, Fig. 8, remains empty. The absorbent must also be saturated, by shaking with gases that are but slightly soluble in it. The saturation of liquids is best done in a flask half filled with the reagent, a rapid stream of gas being led through the liquid, and the flask vigorously shaken. In technical work, where the same analyses are repeatedly made, the absorbent is kept saturated through continual use.

If the pipettes have the temperature of the room, as can be readily determined by introducing a thermometer at *k*, Fig. 9, the analysis is begun by drawing gas into the measuring tube in the manner described in Art. 16. It is convenient to use exactly 100 cubic centimeters, so that the results in percentage may be read off directly. The

apparatus is now arranged as shown in Fig. 9. The pipette is placed on a wooden stand and is connected with the burette by the capillary tube *F*, which is a piece of ther-

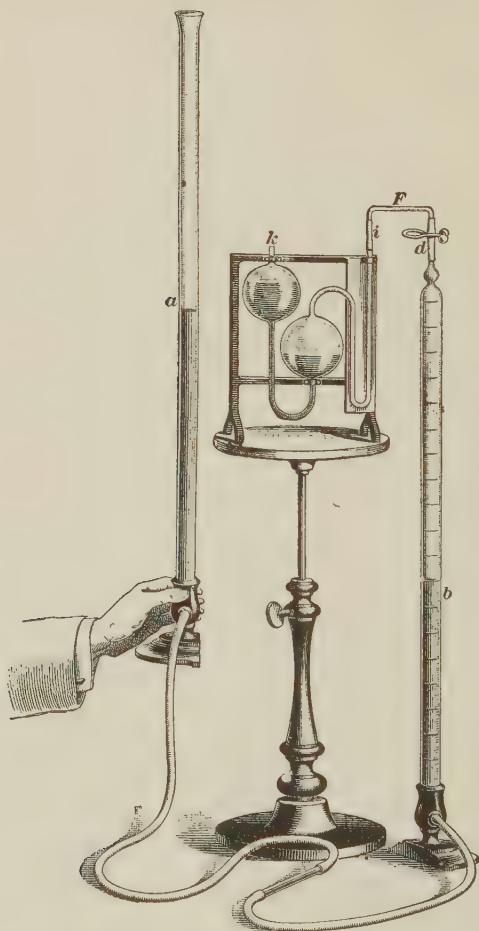


FIG. 9

mometer tubing having a bore of .5 millimeter. To avoid the enclosing of air bubbles, the rubber tube *d* is first filled with water by means of a funnel, and the capillary *F* is then introduced. *F* is thus completely filled with water. The

rubber tube *i* of the pipette is squeezed between the thumb and the first finger of the right hand, and, while thus compressed and free from air, the capillary connecting tube is inserted. On raising the level tube *a* and opening the pinch cock at *d*, the gas passes through the connecting tube into the absorption pipette. Any small air bubbles that may have been enclosed when *F* was inserted into *i* are, at the beginning, separated from the gas by the water in *F*. If these bubbles do not take more than 5 to 10 millimeters of space in the capillary of the pipette, they may be disregarded, since the error arising therefrom is only about .03 cubic centimeter.

If the bubbles are larger, although after a little practice this will seldom occur, the gas is brought back into the burette by lowering the level tube, and the operation is repeated. When the gas has passed over into the pipette, about $\frac{1}{2}$ cubic centimeter of water is allowed to follow, this water serving to rinse the capillary and to free it sufficiently from the absorbing liquid that it previously contained. The gas is now enclosed between two columns of liquid, the absorbent on the one side and the water in the capillary on the other side. The burette, having been closed by the pinch cock, is disconnected, and the pipette is carefully shaken and the absorption of the gas thus effected. The burette and pipette are then reconnected, the level tube is placed on the floor, and the gas is brought back into the burette, care being taken that *none* of the absorbing liquid passes further than the connecting capillary *F*. The pinch cock is closed, and the reading of the remaining volume is made.

27. Double, or Compound, Pipette.—In cases where it is necessary to prevent the reagent from coming into contact with atmospheric air (as, for instance, with alkaline pyregallol, cuprous chloride, etc.), the *double*, or *compound*, *pipette*, shown in Fig. 10, is used. It differs from the pipette shown in Fig. 8, by having two extra bulbs, which, being partially filled with water, serve as a water seal and thus

prevent the reagent from coming in contact with the air. The apparatus consists of the large glass bulb *a*, of about 150 cubic centimeters capacity, and three smaller bulbs *b*, *c*, *d*, each having a capacity of about 100 cubic centimeters.

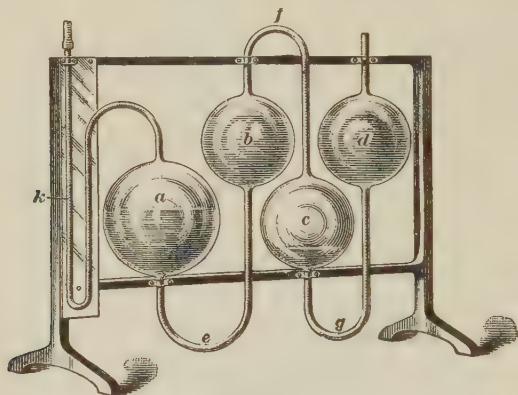


FIG. 10

They are connected by the bent tubes *e*, *f*, and *g*, and end in the bent capillary tube *k*.

The addition of these two extra globes makes it somewhat more difficult to fill this pipette. It is necessary to so arrange matters that, when the absorbing reagent fills the bulb *a*, the water shall occupy *c*, so that, when the reagent passes up into *b*, the water shall be driven into *d*. If this condition is not properly secured, as the reagent is made to pass backwards and forwards between *a* and *b*, air will either be drawn in through the water in the water seal, or else some of the water itself will be drawn over into *b*.

28. Filling the Double-Absorption Pipette.—The following is considered the best method of filling the apparatus: The empty pipette is supported in an inverted position, and an ordinary 10-cubic-centimeter pipette *p* is connected to the capillary tube *k*, as shown in Fig. 11. To the free end of the latter, a piece of narrow glass tube *t* is attached by means of a short piece of rubber tubing provided with a pinch cock *l*. Another short length of rubber tube,

also carrying a pinch cock *n*, is attached to *m*. The air within the apparatus is then swept out by passing a stream of

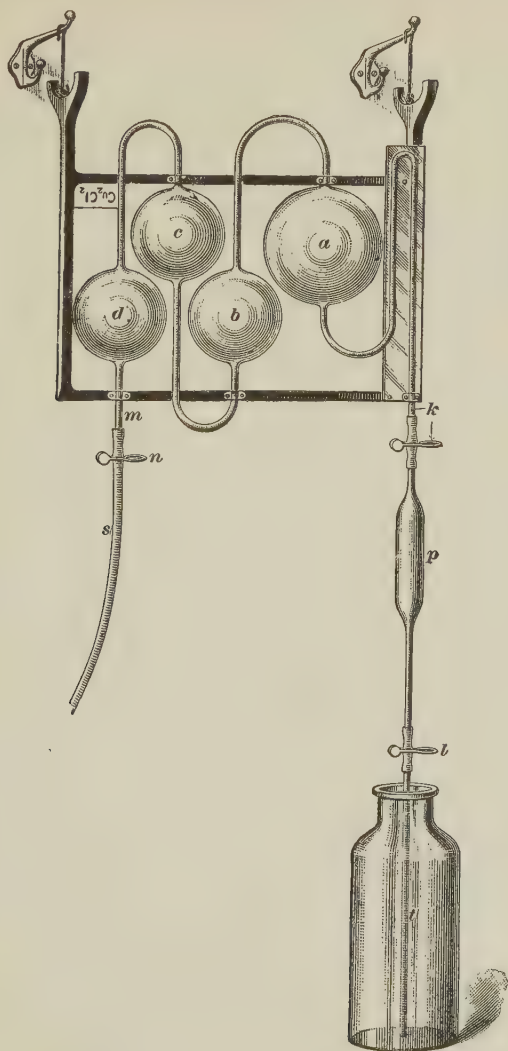


FIG. 11

some inert gas (i. e., inert toward the particular reagent that is destined to fill the pipette), such as nitrogen or carbon

dioxide, for instance. The narrow glass tube *t* is then dipped into the bottle containing the reagent in question, which is drawn up into the apparatus by applying suction through the rubber tube *s*. As soon as the globe *a* is completely filled, care being taken not to draw any liquid over into globe *b*, the clamps *n* and *l* are closed, and the tube *t* disconnected.

The apparatus is returned to its normal position, the little pipette *p* being supported by the hand. The burette, which has been previously filled with the same inert gas used for the pipette, is now attached to the rubber union at *l* by means of the bent capillary tube *t*, as shown in Fig. 12. The

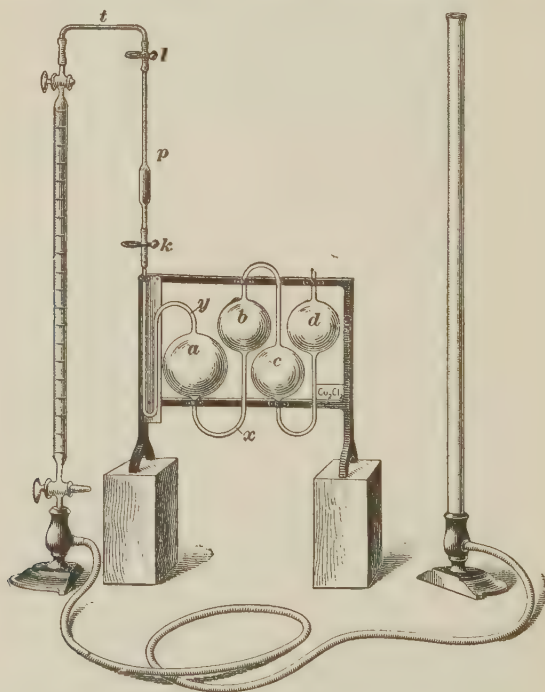


FIG. 12

reagent should now occupy the entire space between the clamp *l* and a point *x* in the bent tube, except probably for a small bubble that, most likely, will have collected at *y*. The rubber tube (see Fig. 11) is now removed, and 3 or

4 cubic centimeters of water are introduced into the globe *d* by means of a thistle funnel. This water will partly descend into the bent tube connecting *c* and *d*. and is intended to serve as a temporary water seal.

The inert gas in the burette is now slowly passed into the pipette by raising the level tube and opening the stop-cock of the measuring tube and the clamps *l* and *k*. As the gas passes in, the reagent is driven from the globe *a* to *b*, while the gas that was in *b* is expelled through the small quantity of water that was in *d*. When all the gas from the burette has been transferred to the pipette, clamp *l* is closed, and water is introduced into the globe *d* until it is nearly filled. The clamp *k* is now closed, and the little pipette *p* removed. The clamp should be opened again just to allow the liquids to sink to their natural level, and the rubber then closed by means of a plug or glass rod. The gas pipette is now properly charged, the space between the reagent and the water seal being occupied by inert gas, while the confining water occupies such a position in the globes *c* and *d* that it will neither pass over into *b* nor allow air to pass through when the reagent is being transferred backwards and forwards from *a* to *b*. The interposition of the 10-cubic-centimeter pipette in the filling operation will have secured the introduction of rather more than enough of the reagent to fill globe *a*. When, therefore, in the process of returning a gas from the absorption pipette to the burette, the reagent completely fills the bulb *a* and capillary tube, there will still remain a few cubic centimeters in globe *b*.

Since 100 cubic centimeters of gas (the capacity of the burette) may at any time be introduced into the globe *a*, it will be evident that the capacity of *b*, *c*, and *d* must not be less than this volume, otherwise they will overflow.

29. Gases Usually Estimated by Absorption.—The gases that are most frequently estimated by absorption in a simple gas pipette, and the reagents employed for this purpose are:

1. *Carbon Dioxide* CO_2 .—This is absorbed by *potassium*

hydrate. Potassium hydrate of a suitable strength to serve as reagent in gas analysis is made up by dissolving 150 grams of caustic potash in 500 cubic centimeters of water. The pipette shown in Fig. 8 is used for the determination.

2. *Carbon Monoxide CO.*—The absorption agent used is *cuprous chloride*. Cuprous chloride being soluble in ammonia as well as in hydrochloric acid, either an acid or an ammoniacal solution may be used. The former is preferable, except under certain circumstances, which are described in Art. 48, when the ammoniacal solution had to be used. The reagent is made up as follows:

(a) *Acid Solution.**—Thirty grams of chemically pure cuprous chloride are added to 50 cubic centimeters of water in a flask, and 150 cubic centimeters of strong hydrochloric acid are added. A few copper turnings or thin strips of copper may be placed in the brownish solution, and the flask corked up for a day or two, when the liquid will become colorless.

(b) *Ammoniacal Solution.*—Twenty grams of cuprous chloride are mixed with 150 cubic centimeters of water in a flask fitted with a perforated cork carrying two tubes, one reaching to the bottom, while the other ends just below the cork. The air is swept out of the flask by a stream of indifferent gas, such as hydrogen or carbon dioxide, after which the exit tube is made dip beneath the water. A stream of ammonia is then passed into the solution until the cuprous chloride has entirely dissolved; but avoid excess of ammonia. This reagent is used in the double pipette, shown in Fig. 10, and care must be taken to expose the reagent as little as possible to the atmosphere while filling the pipette (see Art. 28).

3. *Oxygen.*—Oxygen is absorbed by *alkaline pyrogallol*. The reagent is prepared by dissolving 20 grams of pyrogallol $1:2:3 = C_6H_3(OH)_3$ in 200 cubic centimeters of a potassium-hydrate solution having the same strength as that used for the absorption of carbon dioxide.

* If cuprous chloride is not at hand, the solution may be made by digesting copper oxide with hydrochloric acid (Sp. Gr. 1.1) in a stoppered bottle that is nearly full of copper wire. The dark solution gradually becomes lighter and when colorless is ready for use. The ammoniacal solution may be made from this by adding a slight excess of ammonia.

4. *Hydrocarbons (olefines)*.—Hydrocarbons are absorbed by fuming *sulphuric acid* or *bromine water*. After exposure to either of these reagents, the gas is freed from either sulphur dioxide or from the vapor of bromine by being transferred to another pipette containing potassium-hydrate solution. The tubes of the pipette containing fuming sulphuric acid as reagent must be kept closed by means of a piece of glass rod and rubber tube, when the apparatus is not used.

Benzene vapor is absorbed by sulphuric acid, but not by bromine water. It is also absorbed by fuming nitric acid.

5. *Nitric Oxide*.—Nitric oxide is absorbed by *ferrous sulphate*. The ferrous sulphate is prepared by dissolving 70 grams of ferrous sulphate in 150 cubic centimeters of water. A double pipette is used for this determination. In case a double pipette is not at hand, the absorption can be made in a single pipette, but then, instead of ferrous sulphate, a solution of potassium permanganate, acidified with sulphuric acid, must be employed as absorption agent.

6. *Chlorine, hydrogen sulphide, sulphur dioxide, hydrochloric-acid gas*, and other acid gases are generally absorbed from gaseous mixtures by potassium hydrate.

ABSORPTION OF A GASEOUS MIXTURE

30. As a first exercise in manipulating gas apparatus, it is recommended to make an absorption of a carefully prepared mixture of gases. A mixture of carbon dioxide, oxygen, carbon monoxide, and nitrogen are especially suitable for this purpose, as these gases are constantly met with, associated together in such gaseous mixtures as furnace gases, generator gases, coal gas, water gas, etc.

The mixture is prepared by partially filling (say, about three-fourths) a collection tube similar to that shown in Fig. 7 with air. A small quantity of oxalic acid is heated with strong sulphuric acid in a test tube fitted with a cork and delivery tube, and the mixture of CO and CO_2 thus obtained is collected in the collection tube, previously mentioned, so

as to fill the remaining one-fourth. The tube now contains a mixture of the four gases, oxygen and nitrogen in the air, and CO and CO_2 collected from the decomposed oxalic acid. It will be obvious that the order in which the gases are to be absorbed from a mixture deserves careful consideration, as, for instance, in this case, the oxygen must be absorbed before the carbon monoxide, otherwise the reagent used to absorb the latter gas (cuprous chloride) would be acted on by the oxygen present.

The different gases should be estimated in the following order:

Carbon dioxide, absorbed by means of potassium hydrate.

Oxygen, absorbed by means of pyrogallol.

Carbon monoxide, absorbed by means of cuprous chloride.

Nitrogen, estimated by difference.

31. Preparation of Water Used in Gas Burette.

The water that is used in the gas burette has to be saturated with the gaseous mixture to be analyzed before beginning the analysis, in order to prevent absorption of the mixture during the analysis, and thus obviating the exactness of the result. For this purpose, a stoppered bottle holding about 300 or 350 cubic centimeters is filled with distilled water and inverted in a water trough. About 100 cubic centimeters of the gaseous mixture is bubbled up into the bottle, which is then closed with the stopper, and the gas thoroughly shaken with the remaining water for a few minutes.

Some of this saturated water is poured into the level tube of the gas burette, and the stop-cock at the foot of the measuring tube is turned so as to establish communication between the two tubes. It should be remarked here that this stop-cock must not be touched again through the entire process of the analysis, the passage of the gas to and from the measuring tube and the various pipettes used being entirely controlled by the upper stop-cock of the measuring tube. The bent capillary connecting tube is then attached to the top of the measuring tube, and the latter is completely filled with water by raising the level tube and opening the

stop-cock at the top of the measuring tube, until the liquid drops from the end of the capillary tube. The rubber connection on the collecting tube containing the gas is filled up with a drop of water and joined to the end of the bent capillary (see Fig. 7) and the connections secured with thin binding wire. The level tube is lowered and the pinch cock on the collecting tube and the upper stop-cock of the measuring tube are opened, whereby gas is drawn over into the latter tube. When sufficient gas has thus been transferred, the pinch cock and stop-cock are closed, and the two tubes disconnected. One minute is allowed to elapse for the water to drain down the walls of the measuring tube, when the volume of the gas introduced is read off by lowering the level tube until the level of the water in it and in the measuring tube is the same. The graduation mark that coincides with the bottom of the meniscus represents the volume of gas taken for the analysis.

32. It is convenient to employ, when possible, exactly 100 cubic centimeters of the gas under analysis, in which case the number of cubic centimeters of the various constituents that are absorbed represents the percentage of each ingredient in the gas mixture. If, therefore, more than 100 cubic centimeters have first been introduced into the apparatus, the excess may be removed by raising the level tube until the gas is compressed to exactly 100 cubic centimeters, then, keeping the water in that position by pressing a finger upon the rubber tube, the stop-cock at the top is momentarily opened. This allows the excess of gas to escape, leaving exactly 100 cubic centimeters at atmospheric pressure. This is controlled by again lowering the level tube until the water in each tube is at the same level, when the gas should be found to occupy 100 cubic centimeters.

33. Determination of Carbon Dioxide.—We are now ready to begin the first determination, that is, that of carbon dioxide, and, for this purpose, the burette is attached to the absorption pipette, containing potassium hydrate, in the

manner shown in Fig. 13. Before the two pieces of apparatus are, however, joined, the potassium hydrate solution is drawn up so as to completely fill the globe *a*, and the bent capillary tube to the mark *c*, which is made on the white plate behind it. The pinch cock keeps it in this position. After the rubber connections have been secured with

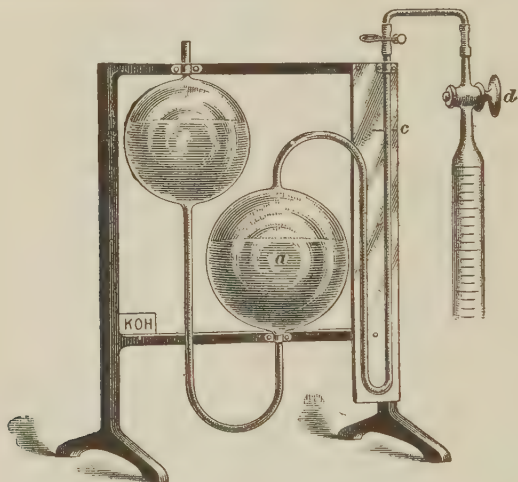


FIG. 13

binding wire, the pinch cock is opened, when, if the joints are tight, the reagent will not sink from its position at *c*. The pinch cock may be kept open by lifting it so that it nips the glass tube. The level tube is now raised (being handled exclusively by its foot) and the stop-cock *d* at the top of the measuring tube is opened.

The gas is thus transferred completely to the bulb *a* of the pipette; 2 or 3 drops of water from the measuring tube are allowed to follow the gas into the bulb (by doing so, the capillary tube of the pipette is washed each time the apparatus is used), after which the stop-cock *d* is closed. The gas is allowed to remain in contact with the potassium-hydrate solution for about 5 minutes, during which time the apparatus is gently shaken so as to moisten the sides of the globe with the reagent. The level tube is again lowered and the stop-cock *d* opened, and thus the gas returned to the measuring

tube. As soon as the potassium-hydrate solution reaches the point in the capillary tube opposite *c*, the stop-cock is closed.

The utmost care should be exercised not to allow the reagent to come in contact with the rubber connections, or to pass into the measuring tube. The pressure tube is then held in such a position that the water stands at an equal level in both tubes, and, after waiting 1 minute for the water to drain down the walls of the tube, the volume that the gas now occupies is read off.

The operation of filling the pipette with the gas is once repeated in exactly the same way as previously described, in order to be sure that all the carbon dioxide has really been absorbed by the reagent, and the volume is again read off at atmospheric pressure. If the two readings agree, the first absorption was complete. For example,

$$\begin{array}{rcl} \text{Original volume of gas} & = & 100 \text{ c.c.} \\ \text{Volume after absorption by } KOH & = & 88 \text{ c.c.} \\ \text{Carbon dioxide} & = & \frac{12 \text{ c.c.}}{100} = 12\% \end{array}$$

34. Determination of Oxygen.--The potassium-hydrate pipette is now detached from the bent capillary tube at the joint immediately above the pinch cock Fig. 13, and replaced by the double pipette containing the alkaline solution of pyrogallol. Before the latter is connected, the reagent is drawn up into the capillary tube to a marked point, which is, as nearly as possible, the same distance from the pinch cock as that on the pipette used for the previous determination. The gas is transferred for absorption exactly as in the former case, and is left in contact with the reagent, with occasional gentle shaking, for 10 minutes. It is then returned to the measuring tube, the same care being taken to bring the reagent exactly to the mark on the capillary tube. The stop-cock is closed, and, after allowing time for the water to drain off the walls of the measuring tube, the volume of the residual gas is read off at atmospheric pressure. For example,

$$\begin{array}{rcl} \text{Volume of gas before absorption of oxygen} & = & 88 \text{ c.c.} \\ \text{Volume of gas after absorption of oxygen} & = & 73 \text{ c.c.} \\ \text{Oxygen} & = & \frac{15 \text{ c.c.}}{88} = 15\% \end{array}$$

35. Determination of Carbon Monoxide.—After finishing the determination of oxygen as described above, the double pipette containing the pyrogallol is disconnected, and replaced by one containing cuprous chloride in acid solution, the reagent being previously drawn over into the capillary tube to a mark in the same relative position as in the two previous cases. The gas is transferred to the pipette and allowed to remain exposed to the reagent; after the lapse of 1. minutes, it is retransferred to the measuring tube of the burette, and its volume determined as previously stated. For example,

Volume of gas before absorption of carbon monoxide	= 7 3 c. c.
Volume of gas after absorption of carbon monoxide	= <u>6 0.5 c. c.</u>
Carbon monoxide	= 1 2.5 c. c. = 12.5%
Volume of residual gas (nitrogen)	= 6 0.5 c. c. = 60.5%

Hence, the composition of the gas under examination is:

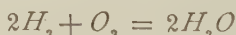
Carbon dioxide	= 1 2
Carbon monoxide	= 1 2.5
Oxygen	= 1 5
Nitrogen (by difference)	= <u>6 0.5</u>
Total	= 1 0 0.0

A duplicate analysis was made, and the correctness confirmed.

ESTIMATION OF GASES BY COMBUSTION

DETERMINATION OF HYDROGEN

36. When hydrogen and oxygen combine according to the equation



the 2 volumes of hydrogen and 1 volume of oxygen practically cease to occupy space, since the volume of the condensed water is inappreciable. By measuring the contraction

of volume that takes place under these circumstances, and multiplying this by $\frac{2}{3}$, the volume of hydrogen that was burnt is determined.

The estimation of hydrogen is then accomplished by mixing a measured volume of the gas with a measured volume of air—rather greater than the volume estimated to be required to furnish the necessary volume of oxygen—and by causing the mixture of hydrogen and oxygen to unite by one of the methods described below. After the combination has been accomplished, the residual gas is again measured, and two-thirds of the contraction will represent the volume of the hydrogen consumed.

Two methods that are mostly used in practical analytical work are given below.

37. Combustion of Hydrogen by Means of Palladiumized Asbestos.—The hydrogen is mixed with an excess of the required volume of air in a gas burette that is attached to a single-absorption pipette charged with distilled water. The capillary tube that forms the connection between the absorption pipette and the measuring tube contains a thread of asbestos upon which has been deposited a quantity of finely divided palladium. As the gas is passed from the measuring tube of the burette to the pipette, it comes in full contact with the palladiumized asbestos (which is gently warmed by means of a small flame), and the hydrogen and oxygen are thereby caused to unite. The gas is finally returned to the burette and measured.

38. Preparation of Palladiumized Asbestos.—The capillary tube containing the palladiumized asbestos is prepared in the following manner: .25 gram of palladium foil is dissolved in as little aqua regia as possible in a small porcelain dish and the solution evaporated to dryness on the water bath. The residue is moistened with 3 or 4 drops of strong hydrochloric acid, and 1 cubic centimeter of water added. The mixture may be gently warmed to complete the solution. To this red-brown solution, when cold, 20 drops

of a cold saturated solution of sodium formate are added. Into this mixture, which will not exceed 2.5 cubic centimeters in volume, .25 gram of asbestos thread is immersed, which will soak up the whole of the liquid. It is self-evident that the thread must be sufficiently fine to admit of being pushed into a capillary tube of 1 millimeter bore. It may be obtained by unraveling a piece of asbestos cloth so as to get single strands. It is cleaned from grease by treating it once or twice with a little carbon disulphide in a test tube and then spreading it out on a clean piece of paper to dry, after which it should be heated for a few minutes on a piece of platinum foil. A quarter of a gram will be about 60 centimeters in length.

A strong solution of sodium carbonate is added by means of a dropper and gently worked into the soaked thread with a glass rod, until the mixture is alkaline, and the dish placed on a water bath. A gentle heat is sufficient to reduce the palladium, which is then precipitated throughout the asbestos as a black deposit. When the contents of the dish are dry, they are rinsed 3 or 4 times with hot water, in order to dissolve out any soluble salts. The thread is then removed and cut into short pieces, each about 4 centimeters long. One of these pieces is straightened out by a gentle twisting of the fingers, and laid on a piece of blotting paper for a few minutes, to remove any superfluous water. It is then introduced into a thick-walled capillary tube, 1 millimeter bore and about 15 centimeters long. When the thread has been pushed a little way into the tube, it may readily be drawn into the middle by applying a gentle suction to the other end. The thread is then dried by gently warming the tube and slowly drawing air through it, after which the tube is bent at right angles, about 3 centimeters from each end. The same piece of palladiumized asbestos may be used for several combustions.

39. Analysis of a Gaseous Mixture of Hydrogen and Air.—As an exercise of this analysis, a mixture of hydrogen and air may be conveniently employed. About

20 cubic centimeters of pure hydrogen are introduced into the gas burette, and the volume accurately measured. The level tube is then lowered, and a quantity of air introduced into the burette until the total volume amounts to between 80 and 85 cubic centimeters; or, in other words, about 60 to 65 cubic centimeters of air are added, and the volume is again accurately measured.

The gas burette is now attached to a single gas pipette charged with water by means of the capillary combustion tube containing the palladiumized asbestos prepared according to Art. 38, instead of the usual connecting tube. The palladium is gently heated by moving a Bunsen flame along the tube, which must be kept warm through the entire operation, so as to prevent water, the product of the combustion of hydrogen and oxygen, from condensing in it. The temperature of the tube, however, must not approach a visible redness. The gas is allowed to pass slowly over the warm palladium, which will be seen to glow at the end toward the incoming gas. When the entire volume of the gas has been passed over into the pipette, it is slowly drawn back again into the burette. This process is repeated once or twice, although, if the palladiumized asbestos is in good order, one repetition is usually sufficient, after which the residual gas is measured. It is then passed once more into the pipette, and back, and measured again. If the two measurements agree, the process is complete. For example,

Original volume of hydrogen taken	= 20.5 c. c.
Excess of air	= <u>63.3 c. c.</u>
Total volume of mixture	= 83.8 c. c.
Volume of combustion	= <u>53.2 c. c.</u>
Contraction	= 30.6 c. c.

$$30.6 \times \frac{2}{3} = 20.4 \text{ c. c.} = \text{volume of hydrogen found}$$

40. For the analysis of marsh gas and similar hydrocarbons, some chemists prefer the apparatus shown in Fig. 14, and which is based on the occlusion of hydrogen by palladium black. The gas burette *A* and the absorption pipette *B*

are joined together by means of the capillary tubes *e, e* and the tube *h*. This tube *h* is about 4 millimeters internal

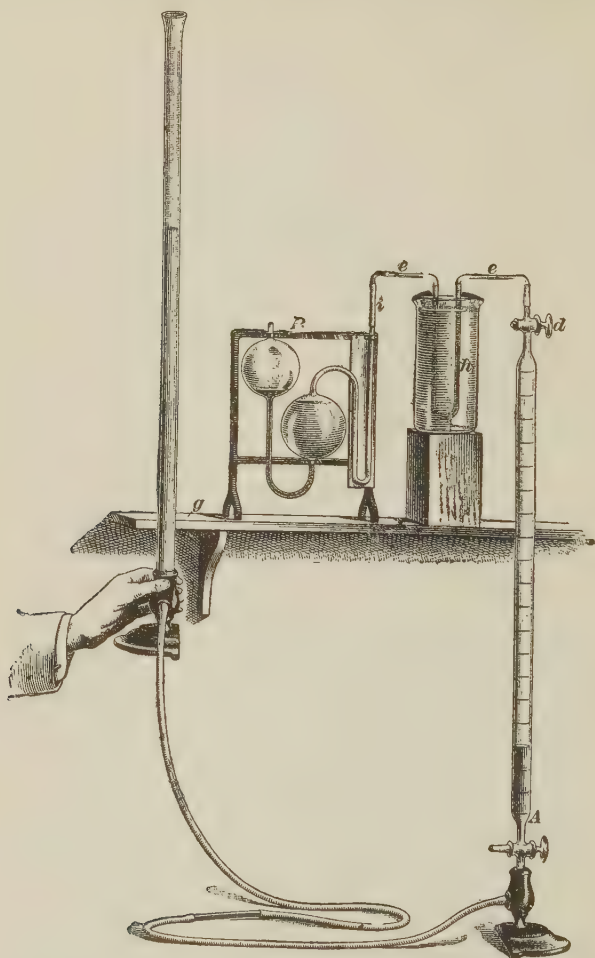


FIG. 14

diameter and 20 centimeters total length, and it contains 4 grams of palladium sponge.

The gas pipette on the stand *g* is filled with water, and its only use, as in the previous arrangement, is to render it possible to repeatedly pass the gas through the tube containing

the palladium. To determine the amount of hydrogen in a gaseous mixture, the gas is measured in the burette joined to the pipette *B*, which is filled with water nearly to *i*. The tube *h* is placed in a good-sized beaker containing water of from 90° to 100° , and, after opening the stop-cock *d*, the gas is driven 3 or 4 times back and forth through the palladium by raising and lowering the level tube.

The hot water is then replaced by water of the temperature of the room, and the gas is again passed twice through the **U** tube, in order to cool it completely. On drawing the gas so far back into the measuring tube that the water in the pipette again stands near *i*, the gas is measured, and the difference between the two measurements, made before and after the absorption, corresponds to the hydrogen plus the amount of air enclosed in the **U** tube when the apparatus was put together. This air volume, with its oxygen contents, may be determined with sufficient exactness once for all by closing, with a piece of rubber tube and glass rod, one side of the tube filled with palladium, cooling the tube to about 9° by placing it in cold water, and then, after connecting it by a capillary with a gas burette completely filled with water, warming it to 100° by placing it in boiling water. The expansion of the enclosed air volume corresponds to a difference of temperature of 91° , i. e., to a third of the enclosed volume of gas.

The palladium is regenerated after the reaction by first leading air over it, whereby it becomes quite hot, removing any drops of moisture that may collect, so that the palladium may easily be shaken out in the form of a dry powder, and then superficially oxidizing the metal by heating it on the lid of a platinum crucible.

41. Combustion of Hydrogen by Explosion With Air.—For this purpose, the mixture of hydrogen with excess of air is transferred to a special piece of apparatus known as an *explosion pipette*, in which are sealed two pieces of platinum wire, whereby the gaseous mixture may be ignited by a spark from a Ruhmkorff coil. One form of these explosion pipettes, in which the gas is confined over water, is shown in

Fig. 15. Water that has been acidulated with sulphuric acid and boiled to expel any dissolved gases is introduced at *a* until the bulb *b* is just full, and the liquid stands level in the other limb. On the tubes *a* and *e*, pieces of thick-walled

rubber tubes are securely wired, and a pinch cock is placed on each. At *d*, two platinum wires are sealed into the glass, between which the electric spark is passed when the gas is to be exploded. In the lower part of the tube at *c*, two platinum electrodes are fused into the glass. These are for the purpose of adding a small quantity of electrolytic gas to the mixture, when the proportion of combustible gas is so small that no explosion will take place when the electric spark is passed.

Before the electrolytic gas is generated, the mixture under analysis is transferred to the measuring tube, which is then detached from the explosion pipette. The two wires from a battery, not from the coil, are then

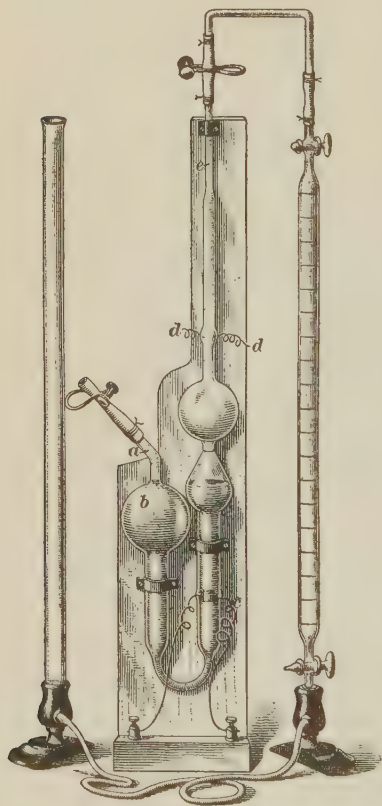


FIG. 15

connected to the electrodes *c* and the oxygen and hydrogen that is evolved is allowed to escape. The current is allowed to pass for about 15 minutes, in order to saturate the water, after which the current is stopped and the liquid driven up to the usual mark on the capillary. The burette is reconnected and the gas returned to the pipette. A small quantity of electrolytic gas is then generated, and thoroughly

mixed with the gas already present before exploding. It is not necessary to know the volume of the gas thus added, as it entirely disappears when fired.

42. As a first exercise in the use of an explosion pipette, a mixture of pure hydrogen and air may be advantageously employed. About 10 to 15 cubic centimeters of hydrogen are introduced into the gas burette, and, after being exactly measured, about 60 to 70 cubic centimeters of air are added, and the mixed gases again measured. The burette is then attached to the explosion pipette, the liquid in the latter being previously drawn up to a mark on the capillary tube *e*. The gas is then passed over into the pipette, and the clamps on the rubber tubes are both closed. The wires from the induction coil are attached to the wires at *d*, and the electric spark allowed to pass. The explosion, although not at all violent, will cause a momentary expansion within the apparatus, but, if sufficient liquid is present, no gas will be driven out of the bulb tube. The thick rubber tube on *a* being closed, the small quantity of air that is in the bulb *b* serves as a cushion, so to speak, at the moment of the explosion, and thus relieves the other part of the apparatus from undue pressure. The moment after passing the spark, the tube *a* is opened, and then the gas is returned to the burette and measured. The contraction represents the hydrogen and atmospheric oxygen with which it has combined to form water, and two-thirds of this shrinkage is the volume of hydrogen that was present. For example,

Volume of hydrogen taken	= 12.5 c. c.
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Volume of air	= 63.3 c. c.
---------------	--------------

Volume of hydrogen and air	= 75.8 c. c.
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Volume after explosion	= 57.5 c. c.
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Contraction	= 18.3 c. c.
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$18.3 \times \frac{2}{3} = 12.2 \text{ c. c.} = \text{volume of hydrogen found}$

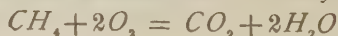
43. For practice in the use of electrolytic gas, the following experiment is recommended: A quantity of air, say 55 or 60 cubic centimeters, is introduced into the burette, and its volume measured in the usual way. The current from

four or five Grove's cells, or its equivalent from any other source, is passed through the dilute acid in the explosion pipette by means of the electrodes at *c*, Fig. 15, for about 10 minutes, and the liquid shaken up once or twice with the gas in order that it may become saturated. The current is then turned off and the liquid drawn up to the mark on the capillary. The burette containing the measured volume of air is attached in the usual manner. About 12 cubic centimeters of electrolytic gas are then generated in the pipette and drawn over into the burette. The actual amount of electrolytic gas that has been added may be ascertained by measuring the total volume of gas in the burette. It is not necessary, however, to know this volume exactly, and a very little practice will enable the student to estimate the volume by the space it occupies in the explosion pipette as it is generated. The mixture of air and electrolytic gas is then passed twice backwards and forwards from the burette, to insure a complete mixing, after which the clamps are closed and the mixture exploded. The residual gas is transferred back to the burette and measured, when the volume should be exactly the same as previously introduced.

Usually, after the first experiment, the volume of the residual air is not exactly identical with that originally taken, owing to the imperfect saturation of the liquid with the various gases. If this is the case, a similar quantity of electrolytic gas should again be added, and the mixture exploded once more after thorough admixture. The volume of the residual gas after this second explosion should then exactly agree with that which was measured after the first operation. The process may be repeated with varying amounts of electrolytic gas, and the volume of the residue will be found to remain constant.

DETERMINATION OF MARSH GAS

44. Explosion of Marsh Gas Over Water.—The product of an explosion of marsh gas (methane) and air is carbon dioxide and water, as is seen from the subjoined equation:



The equation shows that if methane is exploded with air, the volume of CO_2 obtained is equal to the original volume of marsh gas present, and also that 3 volumes present before the explosion are reduced to 1 volume, that of CO_2 , after the explosion. The contraction, therefore, is two-thirds of the original volume of the reacting gases; or, in other words, the contraction is equal to twice the carbon dioxide produced, or to twice the volume of marsh gas exploded.

Owing to the effect of pressure in increasing the solubility of carbon dioxide in water, it is only possible to obtain accurate results when mercury is used as the confining liquid.

45. Determination of Loss of Carbon Dioxide by Solution.—With a view to ascertaining the extent of the loss of carbon dioxide by solution in water, when the explosion is performed over that confining medium, the following experiments were made with the apparatus shown in Fig. 15:

1. 67 cubic centimeters of a mixture of air and carbon dioxide, containing 9 per cent. CO_2 , were introduced into the apparatus and 12 cubic centimeters of electrolytic gas added. After explosion, the remaining volume occupied 66.7 cubic centimeters.

$$\text{Loss of } CO_2 = .3 \text{ c. c.} = .4\%$$

2. 78 cubic centimeters of a similar mixture, containing 20 per cent. CO_2 ; 15 cubic centimeters electrolytic gas added. Volume after explosion = 77.2 cubic centimeters.

$$\text{Loss of } CO_2 = .8 \text{ c. c.} = 1\%$$

3. 50.8 cubic centimeters of a similar mixture, containing 40 per cent. CO_2 ; 15 cubic centimeters electrolytic gas added. Volume after explosion = 49 cubic centimeters.

$$\text{Loss of } CO_2 = 1.8 \text{ c. c.} = 3.5 + \%$$

About the same volume of electrolytic gas was added 3 times, and the mixture exploded and measured after each addition; the volumes obtained were 47.4 cubic centimeters, 46.2 cubic centimeters, and 45.2 cubic centimeters, showing a fairly regular loss of carbon dioxide.

4. 47.2 cubic centimeters of air containing 36.4 per cent. of CO_2 .

(a) 20 c. c. electrolytic gas added; after explosion volume = 45.6 c. c.

(b) 12 c. c. electrolytic gas added; after explosion volume = 45.0 c. c.

(c) 20 c. c. electrolytic gas added; after explosion volume = 43.6 c. c.

(a) loss = 1.6 c. c., or 3.4%

(b) loss = 0.6 c. c.

(c) loss = 1.4 c. c.

Experiments 1, 2, and 3 show that with about the same force of explosion, the loss of CO_2 increases as the percentage rises, while experiment 4 shows that with the same percentage of carbon dioxide, the amount absorbed depends on the force of the explosion.

46. Explosion of Marsh Gas Over Mercury.—An explosion pipette in which mercury is employed is shown in

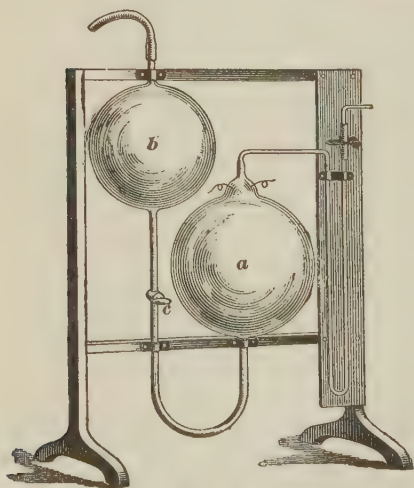


FIG. 16

Fig. 16. It differs from the ordinary absorption pipette only in containing two platinum wires fused in the upper part of bulb *a*, and being furnished with a stop-cock *c*, in order to close the communication between the two bulbs. Before the apparatus is connected to the burette containing the measured mixture for explosion, the mercury is driven over into the capillary tube to a fixed mark by blowing

through the rubber tube on the upper bulb *b*, and, similarly, when the gas is transferred from the burette to the explosion

pipette, it must be drawn over by applying suction to the same rubber tube. The water from the burette should be made follow the gas so as to just fill the capillary tube, but without being allowed to enter the bulb. Before exploding the mixture, both the pinch cock and stop-cock are closed. After the explosion, the gas is transferred to the burette and measured. The explosion pipette is then disconnected and replaced by the simple-absorption pipette containing potassium hydrate, and the carbon dioxide is absorbed in the usual way.

47. Analysis of Mixtures of Hydrogen, Methane, and Nitrogen.—Many gaseous mixtures that constantly come under analysis (such as coal gas, producer gas, water gas, blast-furnace gases, etc.), contain varying quantities of these three gases along with others. After all the other gases have been estimated by absorption in their respective reagents, the hydrogen and marsh gas in the residue are determined by one of the following methods, while the nitrogen is estimated by difference:

48. First Method.—The gas is mixed with an excess of air, and the hydrogen estimated by combustion, by means of palladiumized asbestos, as described in Art. 37. Under these conditions the marsh gas does not burn. The marsh gas is then determined by exploding the residual mixture and absorbing the carbon dioxide produced, as previously described. The volume of nitrogen is found by deducting from the original volume of gas the hydrogen and marsh gas thus determined.

A description of an analysis performed by the writer will make the proceedings clear to the student.

To the action of the following reagents, 100 cubic centimeters of coal gas were exposed:

- (a) Potassium hydrate, to absorb carbon dioxide.
- (b) Alkaline pyrogallol, to absorb oxygen.
- (c) Fuming sulphuric acid, to absorb olefines and benzene vapor.

(d) Ammoniacal cuprous chloride, to absorb carbon monoxide.*

The residual gas, measuring 86.6 cubic centimeters, was returned to the cuprous-chloride pipette, while the burette was disconnected and the water in it (previously saturated with coal gas) was replaced by water saturated with air. Then, 20 cubic centimeters of the gas were transferred to the burette (the rest being reserved for a subsequent experiment), and air was added in more than sufficient quantity for the complete combustion of the hydrogen.

$$\text{Volume of gas} = 20.0 \text{ c. c.}$$

$$\text{Volume of gas} + \text{air} = 64.4 \text{ c. c.}$$

This mixture was then passed over the palladiumized asbestos.

$$\text{Volume after combustion of hydrogen} = 48.2 \text{ c. c.}$$

$$\text{Therefore, } 64.4 - 48.2 = 16.2 \text{ c. c.} = \text{contraction,}$$

$$\text{and } 16.2 \times \frac{2}{3} = 10.8 = \text{volume of hydrogen present in 20 c. c. of gas.}$$

To the residual gas (consisting of marsh gas, nitrogen, and a small surplus of oxygen) an excess of oxygen was added.

$$\text{Volume of residual gas} = 48.2 \text{ c. c.}$$

$$\text{Volume of residual gas} + \text{air} = 69.6 \text{ c. c.}$$

The mixture was then exploded, and the carbon dioxide absorbed.

$$\text{Volume after explosion} = 52.8 \text{ c. c.}$$

$$\text{Therefore, } 69.6 - 52.8 = 16.8 = \text{contraction.}$$

$$\text{Volume after absorption of } CO_2 = 44.4 \text{ c. c.}$$

$$\text{Therefore, } 52.8 - 44.4 = 8.4 = \text{volume of } CO_2 \text{ produced.}$$

Therefore,

$$8.4 \text{ c. c.} = \text{volume of marsh gas present in 20 c. c. of gas.}$$

$$20.0 \text{ c. c.} - (10.8 + 8.4) = .8 \text{ c. c.}$$

$$= \text{volume of nitrogen in 20 c. c. of gas.}$$

* When the absorption of carbon monoxide is to be followed by the combustion of hydrogen with palladiumized asbestos, the ammoniacal solution of cuprous chloride should be used.

Since the original volume of gas taken for analysis was 100 cubic centimeters,

$$\text{then} \quad \frac{10.8 \times 86.6}{20} = 46.76\% \text{ of hydrogen,}$$

$$\text{and} \quad \frac{8.4 \times 86.6}{20} = 36.37\% \text{ of marsh gas,}$$

$$\text{and} \quad \frac{.8 \times 86.6}{20} = 3.46\% \text{ of nitrogen}$$

49. Second Method.—By this method, to the mixture of hydrogen and marsh gas and nitrogen sufficient air or oxygen is added for the complete combustion of both combustible gases, and the mixture exploded. The contraction is then measured, after which the carbon dioxide is absorbed and the volume again measured. From these data, the volumes of the hydrogen and marsh gas can be calculated. As already explained in Art. 44, the contraction due to the combustion of marsh gas is twice the volume of carbon dioxide; if, therefore, the volume of carbon dioxide is ascertained (by absorption with potassium hydrate), and twice this volume be deducted from the contraction on explosion, the product will represent the contraction due to the combustion of the hydrogen.

Let C = contraction on explosion;

C' = volume of CO_2 produced (i. e., contraction on absorption with KOH).

Then, $C - 2C'$ = contraction due to the hydrogen,
and $\frac{2}{3}(C - 2C')$ = volume of hydrogen.

Again, since the volume of carbon dioxide produced is the same as the volume of marsh gas burned,

$C' = \text{volume of marsh gas}$

The following will make this perfectly clear: A portion of the mixture of hydrogen, marsh gas, and nitrogen employed in the previous example (being the residual gas after the removal of the absorbable constituents from a sample of

coal gas) was measured in the burette, and an excess of air added.

$$\text{Volume of gas taken} = 14.2 \text{ c. c.}$$

$$\text{Volume of gas} + \text{air} = 97.6 \text{ c. c.}$$

$$\text{Volume after explosion} = 74.2 \text{ c. c.}$$

$$\text{Therefore, contraction } C = 97.6 - 74.2 = 23.4 \text{ c. c.}$$

$$\text{After absorption by } KOH, \quad \text{volume} = 68.2 \text{ c. c.}$$

$$\text{Therefore, } C' = 74.2 - 68.2 = 6.0 \text{ c. c.}$$

$$\text{Hence, volume of } H \text{ in } 14.2 \text{ c. c. of the gas}$$

$$= \frac{2}{3}(23.4 - 12) = 7.6 \text{ c. c.,}$$

$$\text{and volume of } CH_4 \text{ in } 14.2 \text{ c. c. of the gas} = 6.0 \text{ c. c.,}$$

$$\text{and volume of } N \text{ in } 14.2 \text{ c. c. of the gas}$$

$$= 14.2 - (7.6 + 6.0) = 0.6 \text{ c. c.}$$

Calculating the percentage as in the previous instance,

$$\frac{7.6 \times 86.6}{14.2} = 46.3\% \text{ of hydrogen}$$

$$\frac{6 \times 86.6}{14.2} = 36.5\% \text{ of marsh gas}$$

$$\frac{.6 \times 86.6}{14.2} = 3.6\% \text{ of nitrogen}$$

In cases where the gas under analysis contains a relatively large proportion of nitrogen, as, for example, in the case of producer gas or blast-furnace gases, the addition of air would dilute the gas to such an extent as to render it non-combustible. Under these circumstances, therefore, either oxygen must be substituted for air, or else, after sufficient air has been added to furnish the requisite amount of oxygen, a few cubic centimeters of electrolytic gas may be added to the mixture. The electrolytic gas for this purpose may be generated in the pipette described in Art. 41, and then transferred to the mercury-explosion pipette.

THE NITROMETER AND GASVOLUMETER

50. The **nitrometer** and the **gasvolumeter**, which were invented by Lunge, simplify gas analyses very much, and may be used for many determinations where gases are evolved. They are made in several forms; but only those forms that have given the best satisfaction are described.

The form of gasvolumeter described was designed by Jopp.

The nitrometer, Fig. 17 (a), consists of two glass tubes *e*, *f*, connected by a rubber tube. The tube *e* is provided with a three-way stop-cock *l*, which can be closed, can make connection between *e* and the funnel *g*, or between *e* and the capillary tube *h*. The tube *e* may or may not be graduated; when used in connection with a gasvolumeter, graduation is unnecessary.

The gasvolumeter, Fig. 17 (b), consists of three tubes *a*, *b*, and *c*, connected by rubber tubes and the T tube *d*. The tubes *a*, *b* are graduated, and *a* is provided with a three-way stop-cock opening into the capillary tubes *i* and *j*; *b* is provided with a stop-cock *k*, which, if the apparatus is to be adjusted only once, may be omitted, having the end of *b* simply drawn to a point, which may be closed by fusion. To adjust the apparatus, the thermometer and barometer are read.

The volume that 25 cubic centimeters of standard dry air (at 760 millimeters pressure and 0° C.) will occupy if measured moist at the observed temperature and pressure is calculated, and this calculated volume of air is admitted to the tube *b* at atmospheric pressure and temperature, and the cock *k* closed. The liquid in the tubes *a*, *b*, and *c* is mercury; and since the three tubes are connected, if any volume

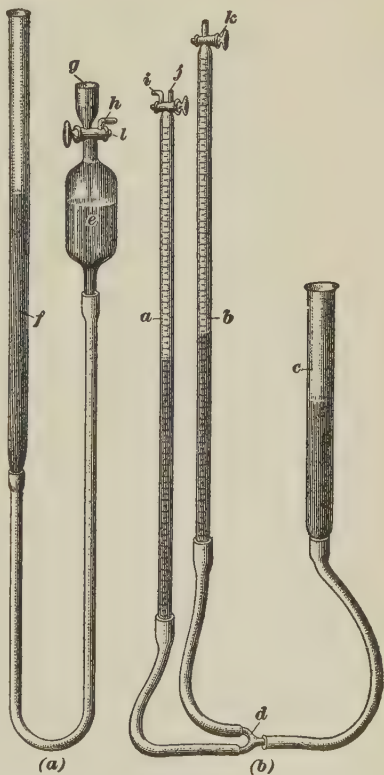


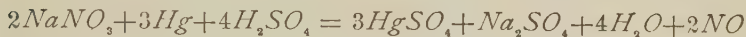
FIG. 17

of gas is confined in a and the pressure tube c adjusted so that the mercury in b stands at the 25-cubic-centimeter mark, and that in a is at the same level, the gas in a will be compressed until it occupies the volume it would occupy if dry and at normal pressure and temperature. It is apparent that if this instrument is substituted for the gas burette and readings made when the mercury in b stands at the 25-cubic-centimeter mark and in a at the same level, the volumes read in a are the volumes the gases would occupy under normal conditions. In this way the rather tedious calculations are avoided.

In making analyses of solid or liquid substances by measuring a gas evolved, it is not alone necessary to know the space that the evolved gas will occupy under normal conditions, but it is also necessary to know how much this gas will weigh. This weight may be calculated by multiplying the number of cubic centimeters by the weight of 1 cubic centimeter; but this calculation may be saved by the gasvolumeter. Take, for example, the gas NO . Twenty-five cubic centimeters of dry NO under normal conditions weigh 33.6 milligrams. If we have NO in the tube a and set the pressure tube c so that the mercury in b stands at 33.6 and in a at the same level, we can read from a the number of milligrams of NO . Obviously similar calculations can be made for any other gases and points can be found on tube b at which the mercury can be set to read milligrams of any gas in tube a .

In making a gas analysis with this apparatus, the gas is measured in tube a , adjusting the pressure so that the mercury in b stands at the 25 mark and in a at the same level. Then turn the stop-cock l of the nitrometer, Fig. 17 (a), so as to open h and by raising f fill e with mercury, close the cock and connect h and i . Lower the tube f and raise tube c . Now, by opening the cocks, the gas can be transferred to e . Close the cocks and disconnect h and i . Pour the absorbing reagent into funnel g and by carefully turning the cock l and regulating with the tube f , introduce the reagent into e . Care must be

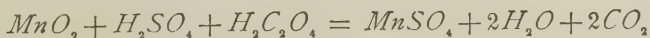
taken to lose no gas and introduce no air here. Close the cock *l* and shake *e* until the absorption is complete. Return the gas to *a* and measure. Nitrates and nitrites are decomposed by large excess of sulphuric acid and mercury according to the equations:



The nitrogen in these compounds can therefore be readily determined with the nitrometer. About .2 gram of nitrate dissolved in 2 cubic centimeters of water is carefully introduced through *g* into *e*, Fig. 17 (*a*). Wash the funnel *g* with 1 cubic centimeter of water, but be careful to admit no air into *e*. Then carefully introduce 5 cubic centimeters of strong sulphuric acid through *g* into *e*, then two lots of 3 cubic centimeters each to rinse thoroughly the funnel *g*. The mixing is effected by tipping the tube *e* and raising and lowering *f*. When the reaction is complete and the apparatus has cooled off, transfer the *NO* to tube *a* and measure, adjusting the mercury in *b* so that it stands at 33.6, and that in *a* at the same level. The number of milligrams of *NO* can then be read from tube *a*.

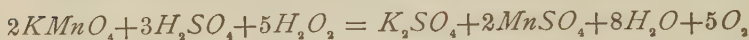
Determinations may sometimes be made by generating gas in an outside vessel, such as a flask, and collecting the gas evolved in *a* or *e* and afterwards transferring to *a*.

The direct estimation of carbonates by evolution of carbon dioxide may be made. The amount of manganese dioxide may be determined by measuring the carbon dioxide evolved by the action of manganese dioxide on oxalic acid in the presence of sulphuric acid, according to the equation:



The available oxygen in manganese dioxide, potassium permanganate, and bleaching powder may be estimated by

measuring the oxygen evolved by the action of hydrogen peroxide according to the equations:



In performing these determinations, the weighed solids are introduced into the flask with water; in the case of manganese dioxide and potassium permanganate dilute sulphuric acid is added. The reagent, which in the three cases mentioned is hydrogen peroxide, is placed in a test tube in the flask. The flask is closed with a stopper carrying a tube and is connected with *h* or *i*. The stop-cock is then turned so as to connect *e* with *g* or *a* with *j*, and the level tube raised so as to fill *e* or *a* with mercury. Then the cock is turned so as to connect *e* or *a* with the flask and the level tube slightly lowered. The flask is tipped so as to empty the contents of the test tube into the liquid in the flask. During the evolution of the gas the level tube is lowered somewhat so as not to have excessive pressure in the apparatus. When all the gas has been evolved, the level tube is raised until the gas in *e* or *a* is under atmospheric pressure, the apparatus is allowed to assume its original temperature, the cock is closed, and the gas measured.

ANALYSIS OF CHIMNEY GASES

51. The analysis of chimney gases is a frequent occurrence in factories and works of all kinds, the percentage (by volume) of oxygen, carbon dioxide, carbon monoxide, and nitrogen being, as a rule, required. The determination of these gases has been already described in the preceding articles, but as especially constructed apparatus are mostly used for this purpose, those which, owing to their convenient form, compactness, and simplicity of manipulating, are most frequently met, will be briefly described in the following articles.

52. Modified Elliott Apparatus.—The modified Elliott apparatus shown in Fig. 18 consists of two glass tubes: *i b*, which has a capacity of about 120 to 130 cubic centi-

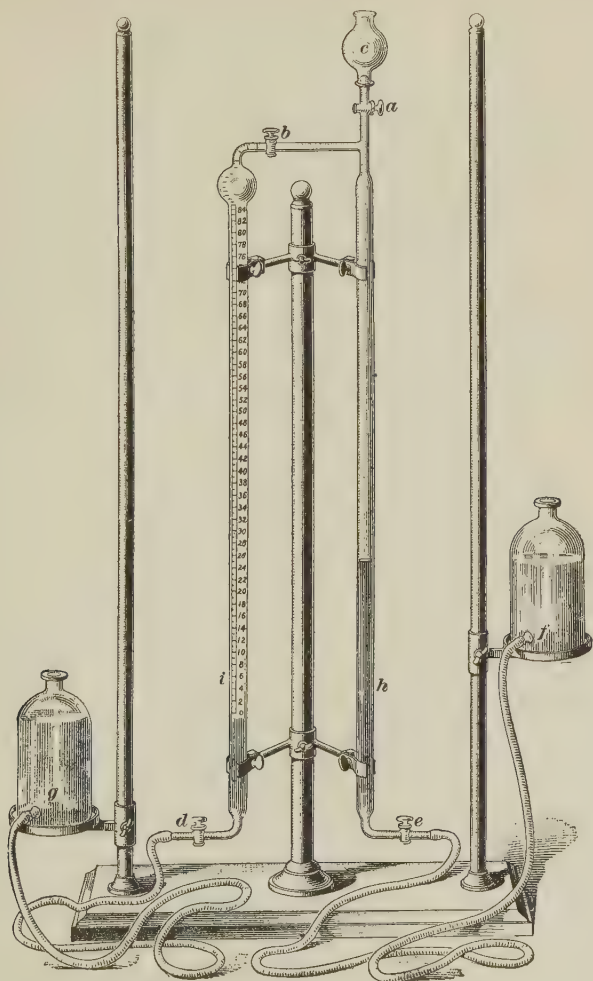


FIG. 18

meters and which is accurately graduated from 0 to 100 cubic centimeters in one-tenth cubic centimeters, and the ungraduated tube *a h*. At *d* and at *e*, a three-way glass

stop-cock connects each of these tubes with a water-supply bottle. The bottles are shown at *g* and *f*.

53. Manipulation of the Apparatus.—The manipulation of the apparatus is as follows: The funnel cap *c* is removed and in its place is connected a glass tube of small diameter; this tube must be of sufficient length to reach well into the flue from which the gas to be analyzed is taken. The stop-cocks *a* and *b* are opened, and the water-supply bottles *f* and *g* are slowly raised until both tubes as well as the glass tube that leads into the flue are filled with water, care being taken that no air remains in the tubes, and that the displacement of water is complete. The cock *b* is closed. The bottle *f* is now gradually lowered which causes the tube *a h* to be filled with gas.

As soon as sufficient gas has been obtained for the analysis, the lower portion of the tube containing water 2 or 3 inches above the point *h*, the stop-cock *a* is closed, the small glass tube reaching into the flue disconnected, and the cap *c* replaced. After the gas is allowed to remain in the tube *a h* for about 15 minutes, to adjust its temperature to that of the room, and thus insuring accurate measurement, the bottle *g* is slowly lowered until the surface of water therein is on an exact level with zero mark on the tube *i b*; the stop-cock *b* is then opened and the bottle *f* gradually raised until a sufficient quantity of gas has been transferred from *h a* to *i b*, which will be indicated by the volume taken, reading from the mark *0* on the graduated tube *i b* to the mark *100* immediately in contact with the stop-cock *b*.

Having thus obtained 100 cubic centimeters of the gas, the stop-cock *b* is closed and *f* is raised until all the remaining gas in *a h* and *a b* is displaced by the water. The first constituent of the gas to be determined is carbon dioxide. The gas is transferred to the tube *a h* by raising *g* and opening *b*, keeping *a* closed and *f* lowered. When the water reaches *b*, the latter is closed. In the funnel cap *c* are placed 50 cubic centimeters of caustic potash. This solution is made by dissolving 280 grams of potassium hydrate in 1,000 cubic

centimeters of distilled water. The stop-cock *a* is partially opened, so that the potassium-hydrate solution in *c* may slowly drop down through the gas in the tube *h* and absorb the carbon dioxide in doing so.

When all but 2 or 3 cubic centimeters of the potassium-hydrate solution has passed through *a*, the latter is closed, thus preventing entrance of any air; *b* is opened, *f* is slowly raised, and *g* lowered. The raising of *f* is continued until the water in the tube *h a* reaches the stop-cock *b* and the latter is immediately closed. The gas is allowed to stand in the tube *i b* five minutes before taking the reading of the volume on the tube, bearing in mind that the level of the water in *g* must be on a level with the water in *i b* to obtain equal pressure. The difference between *O* and the point indicated by the water in the tube *i b* will give the amount of carbon dioxide absorbed from the gas by the potassium-hydrate solution.

Thus original volume indicated = 0.0

After absorption of CO_2 = 12.1

Carbon dioxide = 12.1, or 12.1% carbon dioxide by volume.

To obtain the oxygen, the gas is transferred from *i b* to *a h*, as described before, and in *c* is placed 50 cubic centimeters of an alkaline solution of pyrogallol. A suitable solution is prepared by dissolving 10 grams of pyrogallol in 25 cubic centimeters of distilled water, placing it in *c*, and adding 35 cubic centimeters of the potassium-hydrate solution. This is allowed to pass slowly through *a* and gradually absorbs the oxygen in the gas; *a* is closed before all the liquid passes out of *c*. The operation is once repeated, and the gas transferred in the usual manner to *i b*, where it is measured after it has been resting there for 5 minutes.

Previous reading = 12.1

After absorption of *O* = 18.5

Oxygen = 6.4, or 6.4% oxygen by volume.

Before transferring the residual gas to *a h* for the determination of the carbon monoxide, all the water in *f* and *a h*

must be replaced by fresh distilled water; to do this, the three-way cock *e* and *a* are opened, when the water will run out of *e* and may be caught in a beaker; *f* and *a h* are thoroughly washed 2 or 3 times with water; *e* is closed in such a way that connection with *f* is again established; *f* is filled with fresh water and raised, and, when the tube *a h* is filled up to *a*, the latter is closed and *f* lowered; *g* is then raised and *b* opened, thus transferring the gas to *a h* for treatment with a solution of cuprous chloride to determine *CO*.

A suitable cuprous-chloride solution is prepared by dissolving 30 grams of cuprous chloride in 200 cubic centimeters of hydrochloric acid (Sp. Gr. 1.19) and using 50 cubic centimeters of it, as soon as the solution has approximately obtained the temperature of the room. Experience has shown that a freshly prepared solution is much more effective as an absorbent of *CO* than one that has been standing for some days. In *c* are placed 50 cubic centimeters of this solution, and it is allowed to slowly drop through *a* and absorb the *CO* as it passes through the gas. This absorption should be repeated 2 or 3 times. The heat generated during this absorption often causes such an increase in the volume of the gas that, when the latter is transferred to the measuring tube, inaccurate readings are obtained. To insure accuracy, the following should be observed:

The gas, after fifteen minutes, is transferred in the usual way to *b i* and the water in *f* and *a h* is replaced by fresh water. The gas is then returned to *a h* and a solution of potassium hydrate is placed in *c* and allowed to drop through the gas in *a h*, absorbing all traces of hydrochloric gas. This process is once repeated, the gas returned to *b i*, and, after allowing it to stand for 15 minutes, the volume is accurately measured.

Previous reading = 18.5

After absorption of *CO* = 20.0

Carbon monoxide = 1.5 or 1.5% carbon monoxide.

The nitrogen present is obtained, as in previous experiments, by difference.

Thus, the analysis will read:

Carbon dioxide	=	1 2.1
Oxygen	=	6.4
Carbon monoxide	=	1.5
Nitrogen	=	8 0.0
Total	=	<hr/> 1 0 0.0

In this analysis, no corrections are required for the tension of the aqueous vapor, since the original gas is saturated with moisture, and, during the analysis, all measurements are made over water.

54. Orsat-Muenke Apparatus.—In the writer's opinion, the apparatus that is best adapted for the rapid determination of carbon dioxide, oxygen, and carbon monoxide is the *Orsat-Muenke*; it is readily portable, not liable to be broken, easy to manipulate, sufficiently accurate for all technical purposes, and always ready for use.

The apparatus, shown in Fig. 19, consists of the graduated measuring burette *a*, of 100 cubic centimeters capacity; it is jacketed with water, to prevent changes of temperature affecting the gas volume; the first 45 cubic centimeters are usually divided into one-tenth cubic centimeters, while the remaining 55 cubic centimeters are divided into cubic centimeters only. The burette ends in a thick capillary tube, which is fastened at both ends, at *b* in a cut of the dividing panel, and at *c* by means of a small brace attached to the cover of the case. The capillary tube is bent at its further end and connected with the U tube *d* containing some loose cotton, and at the bend is filled with water in order to retain all dust and to saturate the gas thoroughly with moisture before measuring takes place. The rear end of the three-way cock *e* is connected by means of a rubber tube *f* with the rubber aspirator *g*, which fills the tube with the gas to be analyzed. The absorption of the different constituents of the gas under examination takes place in the U-shaped absorption pipettes *h*, *i*, and *j*, which are connected with the stoppers by short rubber tubes. For the enlargement of the

absorbing surfaces, *h*, *i*, and *j* are filled with glass tubes. Since the mark *k* is above the place of connection, the latter is always moistened by the respective liquid, and, therefore,

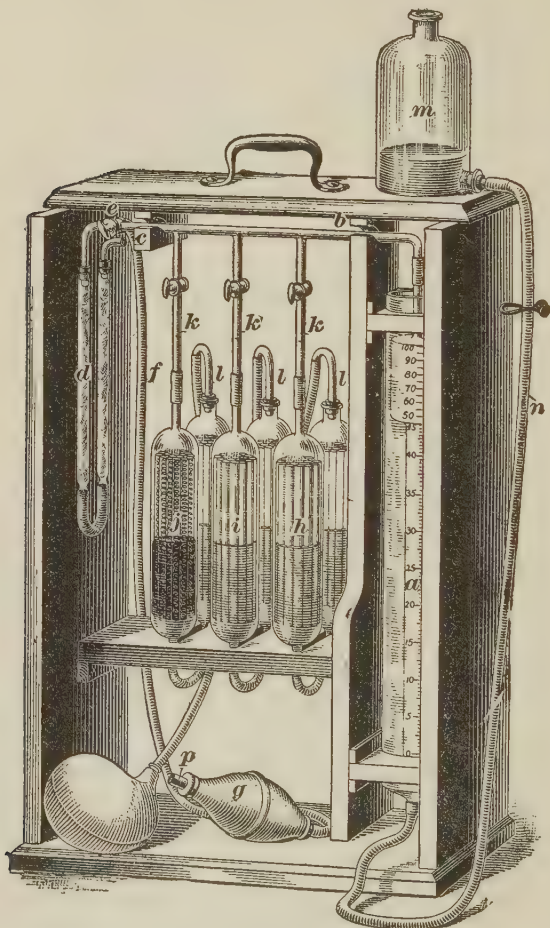


FIG. 19

can easily be maintained air-tight. The other end of the absorption pipettes is closed by a rubber cork, which contains the small tube *l*; the small tubes are all connected to one rubber bulb of about 200 cubic centimeters capacity, in

order to keep out the atmospheric oxygen. The entire apparatus is enclosed in a wooden case.

55. Charging the Orsat-Muenke Apparatus.—The glass jacket surrounding the burette *a*, as well as the bottle *m*, is filled with distilled water. In order to fill the three absorption pipettes, the stoppers are removed, as well as the glass tubes *l* and the rubber aspirator *g*, and 110 cubic centimeters potassium-hydrate solution, Sp. Gr. 1.26, are poured into the pipette *h*, so that the latter is about half full. This is for the absorption of CO_2 . The pipette *i* contains a solution of 18 grams of pyrogallol in hot water, which is poured into it, and then 70 cubic centimeters of potassium-hydrate solution, Sp. Gr. 1.26, are added, whereby the oxygen is absorbed in the gas under examination. The carbon monoxide is absorbed in the pipette *j*, which contains a solution of cuprous chloride made as follows: 35 grams of cuprous chloride are dissolved in 200 cubic centimeters of concentrated hydrochloric acid, 50 grams of copper clippings added, and the mixture allowed to stand in a glass-stoppered bottle for 24 hours.

Each glass tube in *j* contains a spiral of copper wire. To this solution is added 100 cubic centimeters of water, and enough is transferred to *j* to fill it to the required point. The solutions in the rear section of *h*, *i*, and *j* are transferred to the front part of the pipettes, where the absorption of the gases takes place as follows: The three glass stoppers are closed, the stop-cock *e* turned horizontal, and the bottle *m* containing distilled water raised so that the water fills the burette *a*; give a quarter-turn to the left to the stop-cock *e*, so that the second passage leads to the tube *d*, open the stop-cock of the absorption pipette *h*, lower the bottle *m*, and carefully open the pinch cock placed on the tube *n*, so that the potassium-hydrate solution rises to the mark *k*, whereupon the stop-cock is closed.

The reagents of the two other absorption pipettes are raised in an exactly similar way to *k*. The three stoppers with glass tubes *l* are then attached. About 1 cubic centimeter

of water is placed in the tube *d*, loose cotton is placed in both sides, the stopper reinserted and again connected. After filling the burette *a* with water to the 100-cubic-centimeter mark by raising the bottle *m*, the stop-cock is turned so that the connection of the rubber aspirator *g* with the chimney containing the flue gases is brought about through the tube *p*. Aspiration of the gas into the apparatus is now performed by compressing *g* 10 to 15 times, until the whole conductor is filled with gas. This is easily done by compressing *g* with the left hand, closing the attached tube *f* with the thumb of the right hand, and then, on opening the left hand, allowing *g* to expand, raising the thumb again, compressing *g*, etc., until the object is obtained. To fill the burette *a* with the gas, the stop-cock *e* is turned horizontal, the pinch cock of the tube *n* opened, and the bottle *m* lowered until the gas reaches the zero point in *a*, whereupon *e* is closed.

56. Manipulation of the Orsat-Muenke Apparatus.

To determine the carbon dioxide, the stop-cock of the absorption pipette *h* is opened and *m* raised with the left hand, so that on opening the pinch cock of *n* with the right, the gas enters *h*; *m* is lowered again until the potassium-hydrate solution in *h* reaches to about the tube connection under *h*, and once again drives the gas into the potassium-hydrate vessel by raising *m*. This is repeated 2 or 3 times, and the gas returned to the burette *a* by opening the pinch cock of *n*, lowering *m*, and closing the stop-cock of *h*. To measure the amount of absorbed carbon dioxide, the bottle *m* is held next to the burette in such a way that the water stands at the same level in both vessels, the pinch cock of *n* is closed, and the remaining volume of the gas read off. This amount, subtracted from 100 cubic centimeters, gives the amount of CO_2 .

The gas is then passed into the pipette *i* in the same manner as in *h*, the oxygen being absorbed by the alkaline pyrogallate solution. This absorption is repeated 3 or 4 times, and the gas returned to the measuring tube, and the

amount of absorption read off. The gas is then passed into the pipette *j* for the absorption of carbon monoxide. After repeating for a number of times the absorption in *j*, the gas is passed into *h* before measurement in *a* of the absorbed carbon monoxide. This is necessary on account of the vapors of hydrochloric acid retained by the gas after contact with the cuprous-chloride solution in hydrochloric acid. After passing the gas into *h* 3 or 4 times, it is then measured as usual in *a*, the residual gas being nitrogen.

ANALYSIS OF URINE

PRELIMINARY REMARKS

57. A complete analysis of urine is seldom, if ever, required, and, as in the case of water, only certain constituents are determined. Some of these constituents are never present in normal urine, but occur in the urine of patients suffering from certain diseases; hence, the mere presence of these constituents is sufficient to prove the disease, and a qualitative examination serves this purpose. But even in these cases, the quantities of such constituents are required to indicate the progress of the disease, and, consequently, a quantitative examination is necessary. Other constituents are always present in urine, and, in these cases, qualitative determinations would, of course, be useless. The indications obtained in these cases depend on the quantities of these constituents present, and, consequently, a quantitative examination is required. Certain qualitative determinations are sometimes valuable in examining urine, and, consequently, the subject was partially treated in *Qualitative Analysis*, Part 2. All the determinations given there may be used in examining any sample, and the determinations of color, reaction, and specific gravity, which are always made, need not be repeated at this point.

58. Selecting a Sample.—As the total amount of each constituent passed in 24 hours is what a physician ordinarily wants to know, and as the composition of the urine varies greatly at different times during the day, the selection of the sample for analysis becomes a matter of importance. Ordinarily, the best method of obtaining a sample is to collect the total amount passed during the 24 hours. The volume of this should be carefully noted, the whole thoroughly mixed, and then samples taken for the different determinations. Then, knowing the total amount passed, and the amount taken for the determination of each constituent, the quantity of each constituent passed in 24 hours is readily calculated.

The results obtained in examining a sample passed at one time may be misleading, both because the total amount passed is not taken into account, and because the composition of the urine examined may not represent the composition of the whole. A sample passed at another time during the day might contain only half, or might contain double, the amount of a constituent that is contained in this sample. Then, if the total amount of urine passed is not known, we have nothing from which to calculate the quantity of each constituent passed. The amount of urine passed in 24 hours is frequently given as ranging from 1,200 to 1,500 cubic centimeters, but cases have fallen under the writer's observation in which the total amount passed in 24 hours was rather less than 600 cubic centimeters; while, in others, more than 2 liters were passed during the 24 hours. Results calculated on a basis of 1,200 or 1,500 cubic centimeters, in any of these cases, would obviously have been misleading.

While this method of taking a sample should usually be followed, circumstances frequently demand that it be modified in order to obtain more complete knowledge than would be afforded in this way. For instance, samples of urine passed shortly after a meal are sometimes alkaline; while, at other times, the reaction is acid. To learn this, samples passed at different times during the day would need to be tested separately. Sometimes when urine contains a very small

amount of albumin, a sample passed on rising in the morning will not reveal a trace of this substance, but a sample passed a short time after a meal will give a distinct reaction for this constituent, and the same may be said of minute quantities of sugar. The best plan in such cases is to examine two samples, one passed about an hour after dinner and the other passed on rising in the morning.

Whatever method of collecting a sample is employed, it should be remembered that urine decomposes quite rapidly on standing, especially in a warm place; hence, the sample should be kept in a cool place, and should be examined as soon as possible after it is collected. The chemist's duty ends with the accurate determination of the various constituents, and the interpretation of the results obtained falls within the province of the physician; hence, the pathological significance of the different constituents will not be discussed here.

The principal determination made in the examination of urine are color, reaction, specific gravity, sugar, albumin, urea, uric acid, and chlorides. The total quantity passed in 24 hours should also be noted. As the total amount passed in 24 hours is learned by merely keeping all that is passed and measuring it in a graduated vessel, and as the determinations of color, reaction, and specific gravity have already been fully described in *Qualitative Analysis*, it is unnecessary to further treat these determinations here, and we will consequently pass on to the description of the others.

SUGAR

59. A careful qualitative test for sugar should first be made, and if this shows that the urine is free from sugar, the quantitative determination is, of course, omitted. If, however, sugar is found to be present, the next step is to determine its quantity. The quantitative estimation of sugar is accomplished by means of Fehling's solution, but when this is to be used for quantitative determinations, greater care is required in making up the copper solution. Strictly pure

copper-sulphate crystals that have not lost water of crystallization to the amount of 34.639 grams are dissolved in water and diluted to 500 cubic centimeters; 173 grams of Rochelle salts and 125 grams of potassium hydrate are dissolved in water and diluted to 500 cubic centimeters.

60. Determination of Sugar.—When ready to make a determination, thoroughly mix exactly 10 cubic centimeters of the copper-sulphate solution, and an equal amount of the alkaline solution of Rochelle salts. A portion of this solution may be used for the qualitative test. Then measure exactly 2 cubic centimeters of the solution just prepared into a small flask, dilute it to 10 cubic centimeters, and boil it for 15 or 20 seconds, to see that it does not decompose. If it remains clear, add a few drops of a dilute solution of glucose or honey, and again bring the solution to the boiling point, to see if a precipitate forms promptly, thus testing the solution. If the solution decomposes when boiled, or if a red precipitate is not formed when the glucose is added, there is something wrong with the solution, and a new one must be prepared. This will never happen if pure materials are used, and the solution properly made up.

When a solution is obtained that does not decompose on boiling and that gives a precipitate when a few drops of glucose solution are added, rinse out the flask thoroughly, introduce exactly 2 cubic centimeters of the Fehling solution, and dilute it to 10 cubic centimeters with distilled water. Place the flask on a gauze over a burner, and, as soon as the contents commence to boil, remove it, and add a little of the urine under examination from a burette. The amount of urine that it is safe to add at first will be indicated by the qualitative test. Heat the solution just to boiling, remove it from the heat immediately, give it a rotary motion to secure thorough mixing, allow the precipitate to partially settle, and note the depth of the blue color of the solution. Then continue the addition of urine, a little at a time, bringing the solution just to the boiling point after each addition, until the blue color of the solution is just discharged. From

the amount of urine added to just decolorize the solution, calculate the percentage of sugar in the sample.

The calculation is based on the fact that the 2 cubic centimeters of Fehling's solution used are reduced by .01 gram of sugar; hence, the volume of urine required to decolorize the solution contains .01 gram of sugar. As the specific gravity of urine is never very much greater than 1, it is generally assumed in making this calculation that the specific gravity of the sample is 1, or, what is the same thing, that 1 cubic centimeter of it weighs 1 gram. This is never exactly correct, but is sufficiently accurate for practical purposes. Using this as a basis of calculation, if 1 cubic centimeter of the urine is required to discharge the blue color, the sample contains 1 per cent. of sugar; if .5 cubic centimeter is required, the sample contains 2 per cent. of sugar; and if 2 cubic centimeters are required, the solution contains .5 per cent. of sugar. If more accurate results are required, the specific gravity of the urine must be taken into account.

This titration is, in a sense, the reverse of any so far performed, inasmuch as the reagent is measured out, and the sample added; hence, the greater the amount of sample added from the burette, the lower the percentage of sugar indicated. If a sample contains much sugar, it is best to measure exactly 10 cubic centimeters of it into a graduated 100-cubic-centimeter flask, dilute it exactly to the mark with distilled water, and use this diluted sample for the determination. In this case, an appropriate calculation must, of course, be made in reckoning the result.

ALBUMIN

61. **Albumin** occurs in the urine of patients suffering from certain diseases of the kidneys, and the qualitative methods that have been given in *Qualitative Analysis* are sufficient to indicate these. But, in many cases, it is important that the physician should know the relative amount of albumin contained in the urine from day to day, and, for this purpose, quantitative methods are required. At present,

we have no very satisfactory method for the quantitative determination of albumin. Probably the most accurate one is the gravimetric method, in which the albumin is precipitated by heating the sample and adding an acid; but this method is long and troublesome, and the results obtained by one of the shorter approximate methods are frequently accurate enough for practical purposes. Two methods frequently used are here given.

62. Gravimetric Determination.—Measure 100 cubic centimeters of the sample into a beaker, stand it on a gauze over a burner, and, just as it begins to boil, add 10 or 12 drops of nitric acid of 1.2 Sp. Gr. Mix the solution, cover the beaker with a watch glass, allow it to stand undisturbed for at least 12 hours, and then filter through a paper that has been dried at 100° and weighed. Wash the precipitate and filter thoroughly, dry at 100° until a constant weight is obtained, and, from the weight obtained, calculate the percentage of albumin in the sample.

Acetic acid is frequently used instead of nitric acid to precipitate the albumin, and in some ways it is preferable; but in some cases it forms a slimy precipitate that it is almost impossible to filter. The method is tedious at best, and the following method, which yields approximate results, is usually sufficiently accurate for the purpose of comparison:



FIG. 20

63. Determination With Esbach's Albuminometer.—In using Esbach's albuminometer, the albumin is precipitated by an acid mixture and the percentage is indicated approximately by the size of the precipitate. The albuminometer is simply a graduated tube shown in Fig. 20. To make the determination, fill the tube to the mark *U* with the urine to be tested, then add the Esbach reagent to bring the liquid to the mark *R* when the tube is standing in an upright position. Close the tube with the rubber stopper provided

for the purpose, cautiously mix the contents, and allow the tube to stand, undisturbed, in an upright position for 24 hours. The albumin will be coagulated by the acid reagent, and will settle to the bottom of the tube, so that the amount present may be read off.

In mixing the urine and reagent, place the stopper in the tube and slowly invert it, then bring it back to an upright position, and repeat this 10 or 12 times, but do not shake or agitate the liquid violently. Each graduation line at the bottom of the tube indicates 1 gram of albumin in a liter of urine. For example, if the precipitate of albumin reaches to the second line from the bottom, it indicates that 1 liter of the urine contains 2 grams of albumin, or that the sample contains .2 per cent. of this constituent. Knowing the amount of albumin in a liter, and the total amount of urine passed, the amount of albumin passed in 24 hours is readily calculated.

The urine used for this determination should have an acid reaction, and, as albuminous urines are sometimes neutral or even alkaline, the reaction should always be determined before this estimation is commenced. If the urine is found to be neutral or alkaline, pour approximately the amount needed for the determination into a beaker and add acetic acid, drop by drop, while stirring the sample, until a drop of the urine, removed on the stirring rod and brought in contact with blue litmus paper, imparts a red color to it; but avoid a large excess of the acid. More than 3 drops of the acid will seldom be required. This acidulated sample is used for the determination.

The results obtained by this method are more accurate and concordant when only small quantities of albumin are present. Consequently, when the qualitative test indicates a large amount of albumin, it is best to dilute a portion of the sample with distilled water. The amount of water to be added will depend on the amount of albumin in the urine. It is best to dilute the sample until it contains less than 5 grams per liter of albumin. Of course, an appropriate calculation must be made in obtaining the result, in case the sample is diluted in this way.

Esbach's solution, used to precipitate the albumin, is made by dissolving 10 grams of picric acid and 20 grams of citric acid in distilled water, and diluting the solution to 1 liter. The picric acid is to coagulate the albumin, and the citric acid to hold the phosphates in solution. The solution should be kept in a tightly stoppered bottle. As this method only gives approximate results at best, it should be carefully performed. The solution should always be allowed to stand just 24 hours before taking the reading.

UREA

64. As urea is the most abundant solid constituent of urine, and is always present, a qualitative examination for this constituent is never required, but its quantitative estimation is frequently a matter of importance. Methods based on two different principles are largely employed for its determination. The volumetric method proposed by Liebig was used almost exclusively until recently. This method depends on the fact that mercuric nitrate precipitates urea quantitatively. Recently, it has been largely superseded by a process in which the urea is decomposed by an alkaline solution of hypobromite and the nitrogen evolved measured.

A number of forms of apparatus for carrying out this process have been suggested by different chemists. The forms devised by Hüfner and Doremus are described here. It has been objected to the hypobromite process that the results obtained by it are too low, and this is true if the results are calculated from the theoretical composition of urea; but as the results are usually calculated from the amount of nitrogen found by experiment to be liberated by a given weight of urea, this objection will scarcely hold good. At all events, the results obtained by this process are sufficiently accurate for practical purposes. The older process will be described first.

65. Liebig's Method.—For this method, we need a standard solution of mercuric nitrate of such strength that

1 cubic centimeter is exactly equivalent to .01 gram of urea, a saturated solution of pure sodium carbonate, and a barium solution made by mixing 1 volume of a cold saturated solution of barium nitrate with 2 volumes of a cold saturated solution of barium hydrate. A standard solution of mercuric nitrate, made by dissolving 77.2 grams of pure mercuric oxide in nitric acid and diluting to 1 liter with water, will be of the proper strength for use. It is prepared as follows:

Dissolve 78 grams of mercuric oxide in nitric acid; by the aid of heat, evaporate the solution to a syrupy consistency over a water bath, and dilute this syrupy liquid to somewhat less than 1 liter with distilled water. If a precipitate of basic nitrate separates when the water is added, allow it to settle and decant the clear liquid. Then dissolve the precipitate in the least necessary quantity of nitric acid; add this to the main solution, and mix the whole thoroughly, and standardize it against a urea solution of known strength.

For this purpose, dissolve 2 grams of pure urea in distilled water, dilute it to exactly 100 cubic centimeters, and mix it thoroughly. A solution is thus obtained 10 cubic centimeters of which contain .2 gram of urea. Measure exactly 10 cubic centimeters of this solution into a beaker, and slowly introduce the mercuric nitrate solution from a burette while stirring constantly. As the mercuric nitrate falls into the urea solution, it produces a dense precipitate. When the precipitation seems to be nearly complete, remove a drop of the solution from the beaker on a stirring rod, and bring it in contact with a drop of the saturated solution of sodium carbonate placed on a suitable surface. Some chemists use a *spot plate* or porcelain slab for this purpose, while others prefer a piece of glass standing on a black ground.

If the urea is not completely precipitated, there will be no change of color. Continue to add the mercuric nitrate cautiously, testing after each addition, until a yellow color is produced when a drop of the solution is brought in contact with a drop of the sodium carbonate. This indicates that the urea is completely precipitated, and that the solution

contains a trace of mercuric nitrate, which reacts with the sodium carbonate. Note the reading of the burette, and, from this, calculate how much the solution must be diluted. Add water to the solution until, after thorough mixing, just 20 cubic centimeters of it are required to precipitate the urea in 10 cubic centimeters of the solution and give a faint yellow tinge to a drop of sodium carbonate. The solution will now be of such strength that 1 cubic centimeter of it represents .01 gram of urea.

Having, now, an accurately standardized solution of mercuric nitrate, we are prepared to determine the urea in a sample of urine. This is accomplished as follows: Measure exactly 40 cubic centimeters of the urine into a beaker, add 20 cubic centimeters of the barium solution, and stir thoroughly. The barium solution precipitates the sulphates, carbonates, and phosphates. Filter through a dry filter placed in a dry funnel, and receive the filtrate in a dry, clean beaker. If a good quality of filter paper is used, the filtrate should be clear, but if cloudy, it should be passed through the paper a second time. Measure into a beaker 15 cubic centimeters of the filtrate, which, of course, will contain 10 cubic centimeters of the urine, and add standard mercuric nitrate solution from a burette until a drop of the solution, when brought in contact with a drop of sodium carbonate, produces a yellow color of the same depth as that obtained in standardizing the mercuric nitrate solution.

From the quantity of standard mercuric nitrate used, calculate the percentage of urea in the sample, or the amount passed in 24 hours. With normal urine, the specific gravity serves as a guide in making the titration. A number of cubic centimeters of mercuric nitrate approaching the last two figures of the specific gravity, may usually be added before testing for the end of the reaction. Thus, if the specific gravity of the urine is 1.020, it is generally safe to add 18 cubic centimeters of mercuric nitrate before mixing a drop of the solution with sodium carbonate.

The results obtained by this method are usually correct enough for practical purposes, but their accuracy may be

increased by certain corrections and modifications. Those frequently applied are as follows:

If the urine contains more than 1 per cent. of sodium chloride, 2 cubic centimeters are deducted from the total quantity of mercuric nitrate required to produce the yellow color with sodium carbonate before the calculation is made. It has been found by experiment that about this amount of the mercuric solution is used up by the sodium chloride. If still greater accuracy is required, the chlorine is first determined, just enough silver nitrate is added to precipitate it in the sample used, and the silver chloride is filtered off before the barium solution is added. This is a rather troublesome process, however, and is seldom resorted to.

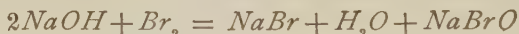
If the urine contains more than 2 per cent. of urea, that is, if more than 20 cubic centimeters of mercuric nitrate are required for its precipitation, a second sample must be titrated after adding to it half as much water as there was mercuric nitrate required in excess of 20 cubic centimeters in the first titration. For instance, if 26 cubic centimeters of mercuric nitrate are added to the first sample, this would be 6 cubic centimeters in excess of 20, and, consequently, 3 cubic centimeters of water must be added to the second sample before titrating it.

If the urine contains less than 2 per cent. of urea, .1 cubic centimeter is subtracted from the total for each 4 cubic centimeters less than 20 of the mercuric nitrate solution used. Thus, if 12 cubic centimeters of mercuric nitrate are required, 8 cubic centimeters less than 20 are used, and, consequently, .2 cubic centimeter must be deducted; hence, 11.8 cubic centimeters of mercuric nitrate should be taken in making the calculation.

If much albumin is present, it interferes with the titration, and should, consequently, be removed. This is done as follows: Measure out exactly 50 cubic centimeters of the urine, add 2 drops of strong acetic acid, and boil the solution a few moments to coagulate the albumin. After allowing the precipitate to completely settle, decant exactly 30 cubic centimeters of the clear solution, add 15 cubic centimeters

of the barium solution, filter off the precipitate, and proceed with the determination as usual. If the precipitated albumin remains at the bottom of the vessel, 40 cubic centimeters of the clear liquid may be decanted and mixed with 20 cubic centimeters of the barium mixture.

66. Determination With Hüfner's Apparatus.—For this determination, we need an alkaline solution of sodium hypobromite. It is made by dissolving 100 grams of sodium hydrate in 250 cubic centimeters of distilled water, and slowly stirring in 25 cubic centimeters of bromine, when sodium hypobromite is formed according to the equation:



Hüfner's apparatus is shown in Fig. 21. The lower bulb *a*, which is fitted into a wooden support, is connected with the bulb *c* by means of a tube containing the stop-cock *b*. The upper part of the bulb *c* is drawn out to a tube, the exterior of which is of ground glass. The perforated glass vessel *d* fits over this tightly, and the graduated tube *e* fits over it loosely inside of the vessel *d*.

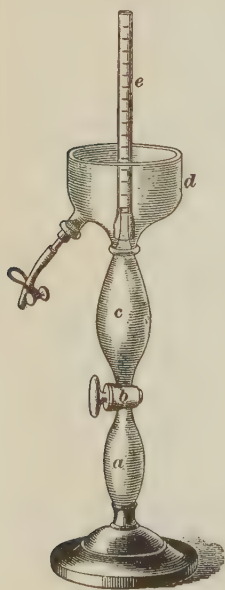
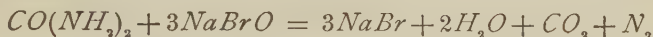


FIG. 21

To determine the urea by means of this apparatus, measure accurately about 2 cubic centimeters of the urine into the bulb *a*, and fill this to the top of the stop-cock with freshly distilled water. Close the connection between the two bulbs by turning the stop-cock, and fill the bulb *c* with equal parts of hypobromite solution and freshly distilled water. Fit the vessel *d* over the tube of the bulb *c*, making sure that the connection is tight, and pour in enough distilled water to cover the end of the tube. Then fill the graduated reading tube with distilled water, and invert it over the tube at the top of the bulb *c*, as shown in the figure. Be sure that the apparatus contains no air bubbles. Now

turn the stop-cock *b*, and allow the hypobromite and urine to mix. The hypobromite immediately attacks the urea, liberating carbon dioxide and nitrogen according to the equation :



The carbon dioxide is absorbed by the excess of sodium hydrate in the hypobromite solution, and the nitrogen collects in the reading tube *e*. When the reaction is complete, and the gas has all collected in the reading tube, transfer this to a vessel of water that has been standing in the room for some time, to acquire its temperature, taking care not to allow any air to enter the tube. After suspending it in this water for a few minutes, bring the level of the water in the tube to the level of that on the outside, and carefully note the volume of nitrogen when the pressure is thus equalized. Then immediately note the temperature and barometric pressure. The urea is then calculated by the formula:

$$W = \frac{100 \ v \ (P - p)}{760 \times 354.33 \ a \ (1 + .00366 \ t)} \quad (5)$$

in which

W = weight, in grams, of urea in 100 cubic centimeters of the urine;

a = volume of urine taken;

v = volume of nitrogen obtained, in cubic centimeters.

t = observed temperature, in centigrade degrees;

P = observed barometric pressure, in millimeters;

p = tension of aqueous vapor for the temperature *t*.

Having now the weight of urea in 100 cubic centimeters of the urine, the amount passed in 24 hours, or the percentage, is readily calculated. In calculating the percentage of urea, the weight of 100 cubic centimeters of urine is of course obtained from the specific gravity of the sample. In handling the reading tube containing the nitrogen, care should be exercised to avoid touching it with the hands more than is necessary, as the warmth of the hand is sufficient to expand the gas and thus cause an error.

It has been found that when the vessel *d* contains water,

the water passing out of the reading tube sometimes carries nitrogen with it, and this is allowed to escape. To avoid this loss, a solution of salt is frequently placed in *d*, instead of water.

67. Estimation With Doremus's Apparatus.—For the determination of urea with the Doremus apparatus, pure bromine and a solution of sodium hydrate are required. The sodium-hydrate solution is made by dissolving 100 grams of the solid in 250 cubic centimeters of water. The apparatus is shown in Fig. 22. It consists of a bulb and

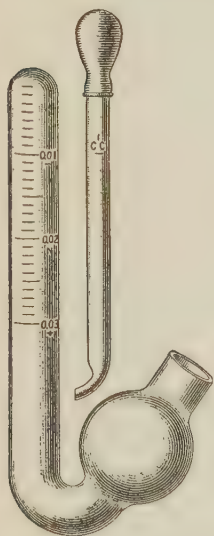


FIG. 22

tube, and a small, curved, nipple-capped pipette, graduated to measure 1 cubic centimeter. The tube of the apparatus is so graduated that each of the small divisions represents .001 gram of urea. On the side of the tube opposite the graduation, two parallel lines are drawn close to each other. To use this ureameter, pour in enough of the sodium hydrate to fill the graduated tube to the parallel lines, then, by means of the nipple pipette, add 1 cubic centimeter of bromine, and when this has completely dissolved, add water to fill the graduated tube and bend up to the bulb.

Mix the solution in the apparatus, and wash the pipette thoroughly. Draw up exactly 1 cubic centimeter of the urine in the pipette, pass the curved end of it through the bulb of the ureameter as far as it will go in the bend, and, by pressing gently and steadily on the nipple, force the urine out into the graduated tube, which is held in a perpendicular position. As soon as all the urine is expelled, withdraw the pipette, taking care not to press the nipple sufficiently to force air out after the urine. When the urine comes in contact with the hypobromite solution, the urea is decomposed the same as in the H \ddot{u} fn \ddot{e} r apparatus.

the carbon dioxide is absorbed by the excess of sodium hydrate, and the nitrogen is collected in the tube, which is so graduated that the nitrogen evolved from 1 milligram of urea just fills one division. After the froth has subsided, read off the number of milligrams of urea contained in the 1 cubic centimeter of urine, and, from this, calculate the percentage or the amount passed in 24 hours.

If preferred, this instrument may be obtained so graduated that each division of the tube represents 1 grain of urea in a fluid ounce of urine. When an instrument thus graduated is used, the weight in grains of urea passed in 24 hours is obtained by multiplying the number of grains indicated by the number of ounces of urine voided. If a number of determinations are to be made, it is handier to make up a quantity of hypobromite solution at once. The solution described for use in the Hüfner apparatus may be mixed with an equal volume of water, and this solution used to fill the tube and bend without further dilution. If only one or two determinations are to be made, however, it is best to prepare the solution in the apparatus, for it must be freshly prepared for use.

This instrument was designed for rapid approximate estimations, but, as it is graduated by experiment at 65° F., the results obtained at this temperature are sufficiently accurate for all practical purposes. In fact, if care is exercised in making the determinations, the results obtained by this method appear to be as accurate as those obtained by other methods, and, on account of its simplicity and the rapidity with which it yields results, this method is very largely used at the present time.

URIC ACID

68. As **uric acid** is quite insoluble, it never occurs in the free state in normal urine, except, possibly, in minute quantities, and, when it is spoken of as a constituent of normal urine, the acid in combination with metals is meant. It occurs in urine combined principally with sodium, potassium, and ammonium, but also with calcium and magnesium. In

health, it is found in quantities ranging from .4 to .8 gram in 24 hours, and usually varies with the urea, of which it is one stage short in oxidation.

Several volumetric methods for the estimation of uric acid have been proposed, but they are all long and cumbersome, and apparently liable to error; hence, the *gravimetric method* is usually employed.

69. Gravimetric Determination of Uric Acid.

Measure 200 cubic centimeters of the sample into a beaker, add 20 cubic centimeters of hydrochloric acid, mix thoroughly, cover the beaker with a watch glass, and stand it in a cool place for 30 hours. During this time, the uric acid will separate, and will be found in crystals at the bottom of the beaker, and on the sides, adhering to the glass. Filter on a paper that has been dried at a temperature ranging from 100° to 105° and weighed, removing the last of the crystals from the beaker by means of a "policeman." Wash thoroughly with distilled water, and note the volume of the filtrate and washings. Place the filter containing the precipitate in an air bath, and heat it at a temperature ranging from 100° to 105° until a constant weight is obtained. It should be dried for 1 hour at this temperature before making the first weighing. To the weight of uric acid thus obtained, add .0038 gram for each 100 cubic centimeters of filtrate and washings, and, from the weight thus obtained, calculate the percentage of uric acid, or the amount passed in 24 hours.

Neubauer finds that 100 cubic centimeters of the filtrate and washings retain .0038 gram of uric acid, and, consequently, advises the addition of this weight for each 100 cubic centimeters of solution in the filtrate, as directed above.

CHLORIDES

70. Chlorine exists in urine chiefly in the form of sodium chloride, but also, in smaller quantities, combined with potassium and ammonium. As most of the chlorine is combined with sodium, it has become customary to calculate it

all to sodium chloride, and report it as such. There are a number of methods for the determination of chlorine in urine, but the one that appears to be the most satisfactory and is most largely employed is the volumetric method devised by Mohr. The details of this process are as follows:

71. Mohr's Method.—Measure 10 cubic centimeters of the sample into a platinum crucible, dissolve from 1 to 2 grams of pure potassium nitrate in it, and slowly evaporate to dryness. Then gradually increase the temperature until the organic matter in the residue is completely burned and a white mass remains, but avoid sudden or long-continued heating, lest chlorine be expelled. Dissolve this saline mass in a little distilled water, wash the crucible with a jet of water from a wash bottle, and allow the washings to run into the beaker with the main solution. When the solution is cool, add dilute nitric acid drop by drop until it has a faint acid reaction, and then add a little pure calcium carbonate to neutralize the excess of acid. Filter off the excess of calcium carbonate and wash the chlorides out of the filter with distilled water. To the filtrate, add a few drops of a cold saturated solution of potassium chromate, and then introduce a standard solution of silver nitrate from a burette, while stirring the solution constantly, until a permanent red color is imparted to it. From the amount of silver solution used to precipitate the chlorine, calculate the weight of sodium chloride in 10 cubic centimeters of the urine, and, from this result, calculate the percentage of sodium chloride, or the amount passed in 24 hours.

A standard solution of silver nitrate of almost any strength may be used for this determination, but, if many determinations are to be made, it is handy to have a solution of such strength that 1 cubic centimeter of it represents .01 gram of sodium chloride. This solution may be prepared by dissolving 29.06 grams of pure silver nitrate in distilled water and diluting the solution to 1 liter, but it is better to standardize it against a solution of sodium chloride, as described under Examination of Water.





